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Analysis of the NBS (Nationl Bureau of Standards) Sediment by the MRI (Midwest Research Institute) Sludge Protocol

Midwest Research Inst., Kansas City, MO

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An extraction technique, involving homogenization of a sediment sample with dichloromethane at dual pH and phase separation by centrifugation, was used in the determination of fifty-one organic priority pollutants as identified in a standard reference sediment sample. These compounds were spiked into the sediment and equilibrated for a defined period of time. The extraction was performed first at pH >11 to isolate the base/neutral compounds; acidic compounds were extracted at pH <2. The extract containing the base/neutral compounds was fractionated by gel permeation chromatography (GPC). Separation and identification of individual compounds in the silica gel fractions was accomplished by gas chromatography/mass spectrometry (GC/MS). Method precision and accuracy are discussed. Tentative identifications of other organic compounds found in the sediment are given.

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ANALYSIS OF THE NBS SEDIMENT BY THE MRI SLUDGE PROTOCOL

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory (EMSL) - Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water.
- Conduct studies to determine the response of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This report discusses the evaluation of the applicability of an interim U.S. EPA protocol for organic compounds in sludges to a standard reference sediment from the National Bureau of Standards. Both the quantitative aspects of the methodology and the qualitative characteristics of the reference sediment are presented.

Robert L. Booth

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ABSTRACT

An extraction technique, involving homogenization of a sediment sample with dichloromethane at dual pH and phase separation by centrifugation, was used in the determination of fifty-one organic priority pollutants as identified in a standard reference sediment sample. These compounds were spiked into the sediment and equilibrated for a defined period of time. The extraction was performed first at pH>11 to isolate the base/neutral compounds; acidic compounds were extracted at pH<2. The extract containing the base/neutral compounds was fractionated by gel permeation chromatography (GPC). Separation and identification of individual compounds in the silica gel fractions was accomplished by gas chromatography/mass spectrometry (GC/MS). Method precision and accuracy are discussed. Tentative identifications of other organic compounds found in the sediment are given.

PREFACE

This is the final report for EPA Contract No. 68-03-2711, "Analysis of the NBS Sediment by the MRI Sludge Protocol," conducted at Midwest Research Institute, Project No. 4586-A(4). The project was directed by Dr. Viorica Lopez-Avila. The work was performed in the Environmental Analysis Section, Dr. John E. Going, Section Head, under the supervision of Dr. James L. Spigarelli, Director of the Analytical Chemistry Department.

This report was written by Dr. Viorica Lopez-Avila. Technical support for the project was provided by Mr. Raymond V. Northcutt, Mr. Jon Onstot, and Ms. Margie Wickham.

MIDWEST RESEARCH INSTITUTE

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August 31, 1981

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SECTION 1

SUMMARY

The objective of this research was to evaluate the application of the extraction, cleanup/fractionation, and analysis procedures of the MRI sludge protocol (see Appendix A) to a sediment standard reference material from National Bureau of Standards (NBS), SRM No. 1645. The evaluation studies were conducted using a set of compounds selected to represent the Environmental Protection Agency's (EPA) priority pollutants. The test compounds were spiked into the sediment sample and incubated for a defined period of time to mimic the environmental conditions. Base/neutral/pesticide compounds were isolated from the sediment matrix by homogenization with methylene chloride at $pH > 11$ followed by centrifugation. Acidic compounds were extracted at $pH < 2$. Extracts containing the base/neutral/pesticide compounds were fractionated by silica gel chromatography and extracts containing the acidic compounds were fractionated by gel permeation chromatography. All analyses were done by capillary gas chromatography/mass spectrometry (GC/MS). Unspiked levels and the precision and accuracy results are reported only for the test compounds. In addition, elution patterns and recoveries of the base/neutral/pesticide test compounds from spiked blanks by silica gel fractionation and the acidic compounds by gel permeation chromatography are reported.

The GC/MS analyses of the four silica gel fractions generated from the NBS sediment extract by silica gel cleanup/fractionation and of the acidic sediment extract resulted in the tentative identification of 106 base/neutral compounds and 11 acidic compounds, without considering the various isomers of many compounds. A comprehensive list of these compounds, grouped by chemical class, is given.

Since the EPA/National Institutes of Health mass spectral data base[1] contains a limited number of compounds, the identifications assigned to the peaks in the NBS sediment extract are considered tentative even for those compounds with large FIT and PURITY indices in the library searches. Confirmed identifications were reported only for those compounds which had identical GC retention times and mass spectra with authentic compounds analyzed under identical gas chromatographic conditions.

SECTION 2

CONCLUSIONS

1. The MRI sludge protocol can be used successfully to analyze for many nonpolar and weakly polar organic priority pollutants spiked into the NBS standard sediment and diluted with organics-free water to mimic a sludge sample. Many polar or reactive compounds containing nitro or epoxy groups were not amenable to the analysis procedures chosen for evaluation.

2. Cleanup/fractionation of the sediment extract containing base/neutral/pesticide compounds by silica gel chromatography and of the acidic sediment extract by gel permeation chromatography reduces sample complexity, improves quantitation of the EPA's priority pollutants, and has no significant effect on recovery for most of the test compounds.

3. When complete sample characterization is required, simultaneous screening of the silica gel fractions with gas chromatographic detectors, both nonselective and element-selective, is helpful in establishing the gas chromatographic conditions for the GC/MS analysis, and provides additional information with regard to the chemical functionalities in the sample components.

4. The excellent resolution and inertness of the fused silica capillary column provided clean mass spectra and thus more reliable identifications for the sample components.

5. Most mass spectral identifications of nonpriority pollutants reported here should be considered tentative since there was no comparison of the chromatographic retention data and mass spectral information of identified constituents with authentic compounds.

6. Most of the compounds tentatively identified in the sediment extract were polycyclic aromatic hydrocarbons, alkyl-substituted polycyclic aromatic hydrocarbons, sulfur-containing heterocyclics, and alkyl substituted sulfur-containing heterocyclics. A few priority pollutants were identified in the NBS sediment extract; their identities are considered confirmed since their GC retention times and mass spectra matched those of authentic compounds analyzed under identical conditions.

7. Quality assurance protocols such as those established in the MRI sludge protocol must be followed thoroughly. Particularly important are capillary column performance tests and instrument calibration since they contribute equally to the quality of the data generated.

SECTION 3

RECOMMENDATIONS

1. For more accurate quantitation of the sample components, the spiking levels should be decided based upon the concentrations of components in the unspiked sample.

2. To avoid overloading the capillary column, an effect that was observed to cause double peaking and leading peaks, wider bore fused silica capillary columns with a thicker layer of liquid phase (0.5 to 1 μ) are recommended for future developmental studies.

3. Evaluation of the reproducibility of splitless injection techniques with real environmental samples, in addition to standard test mixtures, is necessary since lower response factors for internal standard (d_{10}-anthracene and d_{12}-chrysene) were observed in sediment extracts than in standard test mixtures. Hence, other injection techniques, such as on-column injection, should be evaluated.

4. Benzidine could not be detected in any of the standard test mixtures at ≦ 40 ng on column injection. Consequently, if detection limits at such levels are required, other analysis procedures should be evaluated.

5. Several polar compounds (3,3'-dichlorobenzidine, endosulfan sulfate, endosulfan, and endrin) and two acidic priority pollutants (2,4-dinitrophenol and 4,6-dinitrocresol) could not be detected at levels of 4,000 ng/g and below. Consequently, if such levels are required for analysis, other analysis procedures should be investigated. High pressure liquid chromatography with ultraviolet detection or with electrochemical detection is recommended.

6. The sediment sample was a relatively homogeneous sample with particles < 180 μ. Thus, for the successful application of the homogenization/centrifugation procedure, the sediment sample may require some form of pretreatment, such as drying or sieving, prior to the extraction step.

SECTION 4

INTRODUCTION

The primary objective of this research was to evaluate the MRI sludge protocol using a sediment standard reference material, NBS SRM No. 1645, as the sample matrix. By use of a standard reference material, such as this sample matrix, any errors that might be associated with the sample heterogeneity are minimized and interlaboratory comparison of the data is facilitated. The purpose of the evaluation study was twofold:

1. Apply the procedures described in the MRI protocol, or perform minor modifications, if necessary, to analyze for the presence of organic compounds in a sediment standard reference material.

2. Determine method precision and accuracy using the test compounds given in Table 1, spiked into the sediment matrix at two levels.

This information will help the U.S. Environmental Protection Agency (EPA) in its efforts to standardize analytical methodology for environmental sediment samples and to determine the best and most cost-effective analytical methodology for environmental sediment samples.

The standard reference material was prepared from material dredged from the bottom of Indiana Harbor Canal near Gary, Indiana. The material was screened to remove foreign objects, freeze-dried, and sieved (particle sizes < 180 μ). The material was sterilized by radiation to minimize biological activity. A gross characterization of the material, done by NBS,[2] is listed below:

Kjeldahl Nitrogen	0.0797% ± 0.0048
Total Phosphorus	0.051% ± 0.0014
Loss on Ignition (800°C)	10.72% ± 0.28
Oil and Grease (Freon)	1.71% ± 0.26
Chemical Oxygen Demand (Dichromate)	149,400 mg/kg ± 9,000
Mineralogical Characterization	SiO_2 51%; MgO 4%; Al_2O_3 4%; CaO 4%
Total Organic Carbon*	30,000 mg/kg

The successive sections of this report describe the sample analysis procedures, the results of the recovery studies, and the tentative identifications of components in the NBS sediment extract.

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* Done at MRI.

TABLE 1. COMPOUNDS SELECTED FOR RECOVERY STUDIES

Base/Neutrals

Bis(2-chloroethyl) ether
1,3-Dichlorobenzene
1,2-Dichlorobenzene
Hexachloroethane
N-Nitroso-di-*n*-propylamine
Nitrobenzene
Bis(2-chloroethoxy)methane
1,2,4-Trichlorobenzene
Naphthalene
Hexachlorobutadiene
Hexachlorocyclopentadiene
2-Chloronaphthalene
Acenaphthylene
2,6-Dinitrotoluene
Acenaphthene
2,4-Dinitrotoluene
Fluorene
4-Chlorophenyl phenyl ether
Diethylphthalate
4-Bromophenyl phenyl ether
Hexachlorobenzene
Phenanthrene
Anthracene
Di-*n*-Butylphthalate
Fluoranthene
Pyrene
Benzidine
Endosulfan sulfate
Butylbenzylphthalate
Chrysene
3,3'-Dichlorobenzidine
Bis(2-ethylhexyl)phthalate
Benzo[*a*]pyrene
Dibenzo[*a*,*h*]anthracene

Phenols

Phenol
2-Chlorophenol
2,4-Dimethylphenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
2,4-Dinitrophenol
4-Nitrophenol
4,6-Dinitro-*o*-cresol
Pentachlorophenol

Pesticides

Aldrin
Heptachlor epoxide
p,*p*'-DDE
Endrin
p,*p*'-DDD
p,*p*'-DDT
α-Endosulfan
γ-BHC

SECTION 5

SAMPLE ANALYSIS

SCREENING OF THE SEDIMENT EXTRACTS WITH GAS CHROMATOGRAPHIC SELECTIVE DETECTORS

Screening of the silica gel fractions of the NBS sediment extract with gas chromatographic detectors was done primarily to determine the complexity of the sample and to establish the gas chromatographic conditions for GC/MS analysis. These detectors were flame ionization detector (FID), electron capture detector (ECD), nitrogen phosphorus detector (NPD), and Hall™ electrolytic conductivity detector. Two gas chromatographic systems were set up for simultaneous detection using FID/ECD and NPD/Hall™. This allowed increased sensitivity and provided additional information for the identification of components in the sample.

Experimental

Details on the extraction and cleanup procedures are given in the following subsection. The gas chromatographic conditions are listed in Tables 2 and 3. Figure 1 shows the effluent splitter used to connect the fused silica capillary column with the two gas chromatographic detectors. A slightly modified effluent splitter was used for the NPD/Hall™ combination. The split ratio was determined by measuring the flow rates of the combined carrier gas/makeup gas at the exits of the detector towers for the FID and ECD detectors, or at the exit of the detector channels for the NPD and Hall™ detectors. The splitting ratio was found to range from 0.98 to 1.06 when measured at room temperature.

Results and Discussion

Figures 2 through 5 show the FID/ECD chromatograms for the Fractions I through IV, respectively, and Figure 6 shows the FID/ECD chromatogram for the combined Fractions II, III, and IV. The corresponding NPD/Hall™ detector chromatograms for Fractions II, III, and IV are given in Figures 7, 8, and 9, respectively.

TABLE 2. GAS CHROMATOGRAPHIC FID/ECD ANALYSIS

Instrument:	Varian 3700 gas chromatograph equipped with Model 2110 Varian effluent splitter
Column:	30 m x 0.25 mm ID fused silica capillary column coated with SE-54 (J & W)
Temperature program:	50°C (4 min) to 300°C (10 min) at 4°C/min (base/neutral/pesticide compounds) 60°C (5 min) to 325°C at 8°C/min (acids)
Injector temperature:	270°C
Detector temperature:	350°C
Carrier gas:	Prepurified nitrogen at 20 psi (0.7 ml/min)
Makeup gas:	Prepurified nitrogen at 60 ml/min (30 ml/min to FID; 30 ml/min to ECD)
Effluent splitter ratio (FID/ECD):	1:1
Splitless injection:	30 sec
Injection volume:	1.0 to 2.0 µl
Solvent:	Hexane Methanol

TABLE 3. GAS CHROMATOGRAPHIC NPD/HALL™ ANALYSIS

Instrument:	Tracor 560 equipped with Model 702 NPD and Model 700-A Hall™ and modified Model 2110 Varian effluent splitter
Column:	15 m x 0.25 mm ID fused silica capillary column coated with SE-54 (J & W)
Temperature program:	60°C (5 min) to 300°C at 4°C/min
Injector temperature:	250°C
Detector operating conditions:	
700-A Hall™ (nitrogen mode)	
Detector base temperature:	290°C
Reactor temperature:	810°C
Reaction gas:	Hydrogen (UHP) at 60 ml/min
Vent time	0.75 min
Solvent:	Propanol/water (50:50)
Solvent flow:	0.8 ml/min
Resin:	IRN 150:IRN 78 (1:2)
Scrubber:	KOH
NPD	
Detector base temperature:	290°C
Bead temperature:	800°C
Polarizing voltage:	150 V
Air flow	125 ml/min
Hydrogen (UHP) flow:	2.5 ml/min
Desensitizer setting:	30 sec
Carrier gas:	Helium (UHP) at 20 psi (0.7 ml/min)
Makeup gas:	Helium (UHP) at 60 ml/min (30 ml/min to NPD and 30 ml/min to Hall™)
Effluent splitter ratio: (700-A Hall™:NPD)	1:1
Splitless injection:	30 sec
Injection volume:	1.0 to 2.0 µl
Solvent:	Methanol
Attenuation:	10 x 20 (Hall™) 10 x 16 (NPD)

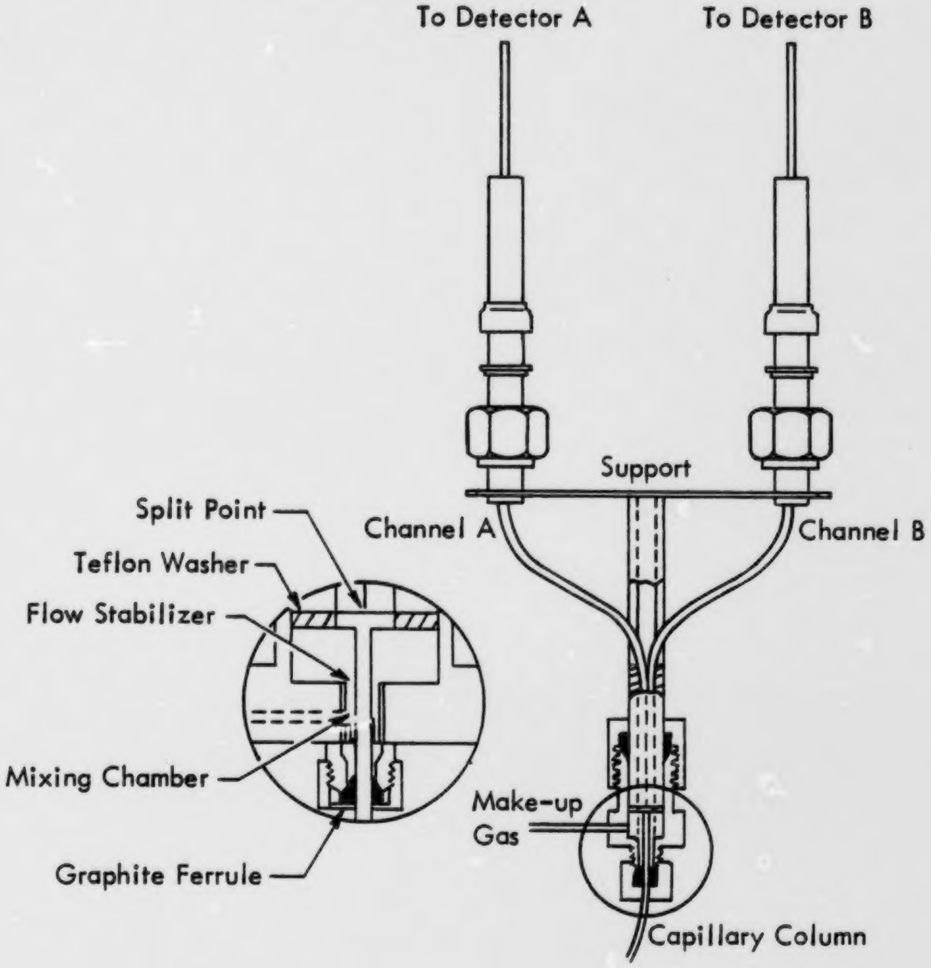
To Detector A
To Detector B
Support
Split Point
Channel A
Channel B
Teflon Washer
Flow Stabilizer
Mixing Chamber
Make-up Gas
Graphite Ferrule
Capillary Column

Figure 1. Varian capillary column effluent splitter.

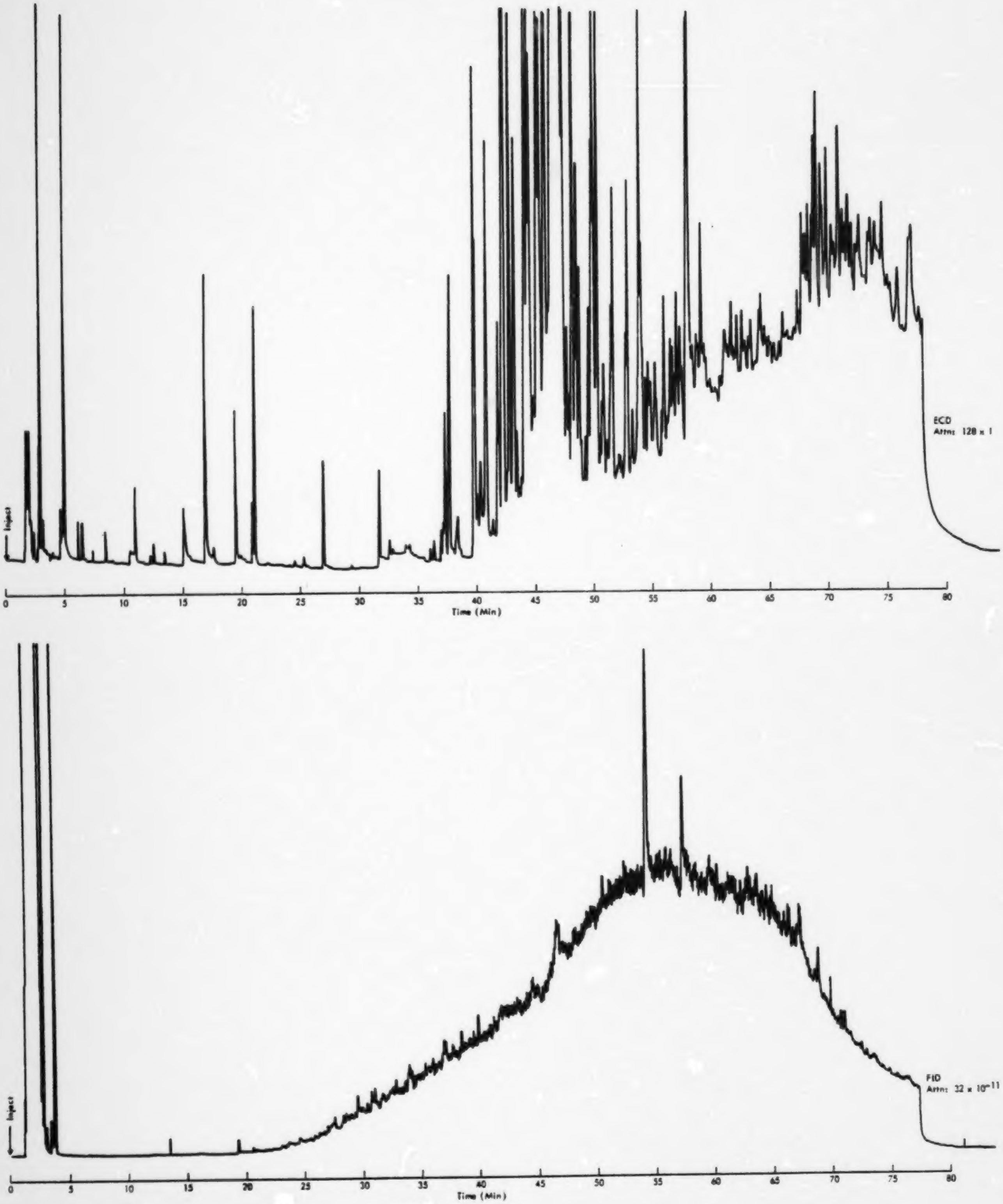

Figure 2. Capillary FID/ECD chromatogram of fraction I obtained by silica gel cleanup/fractionation of the NBS sediment extract.

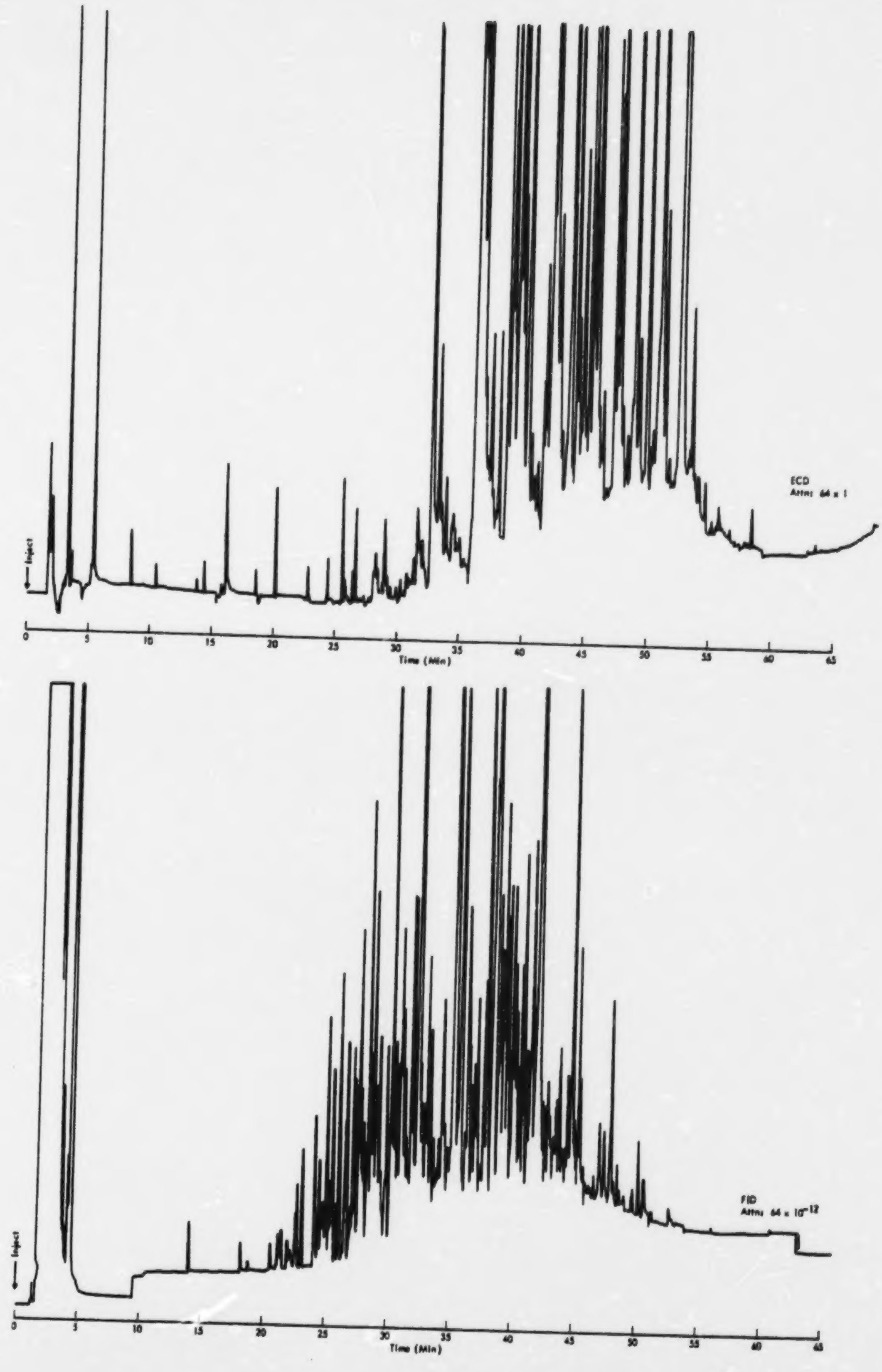

Figure 3. Capillary FID/ECD chromatogram of fraction II obtained by silica gel cleanup/fractionation of the NBS sediment extract.

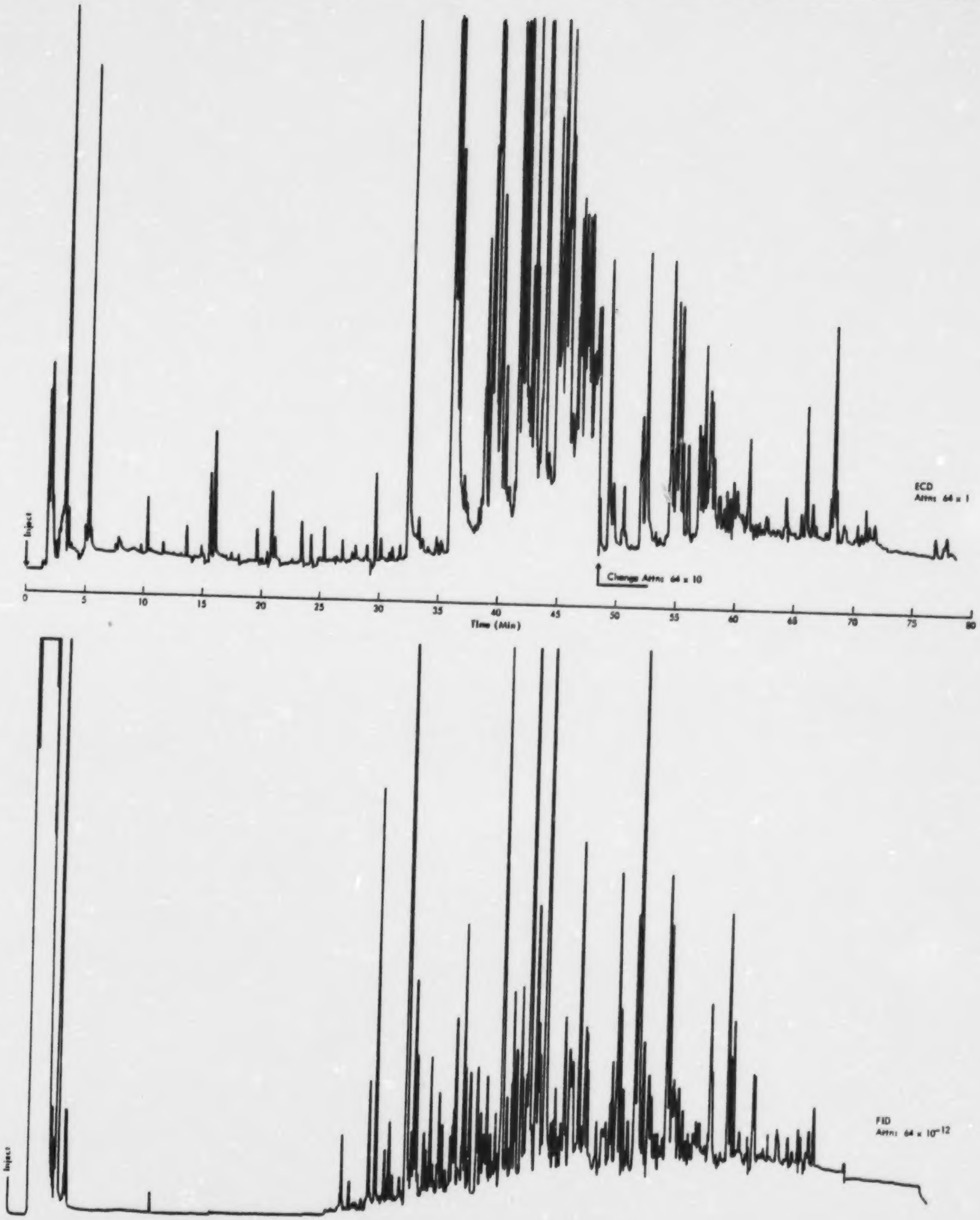

Figure 4. Capillary FID/ECD chromatogram of fraction III obtained by silica gel cleanup/fractionation of the NBS sediment extract.

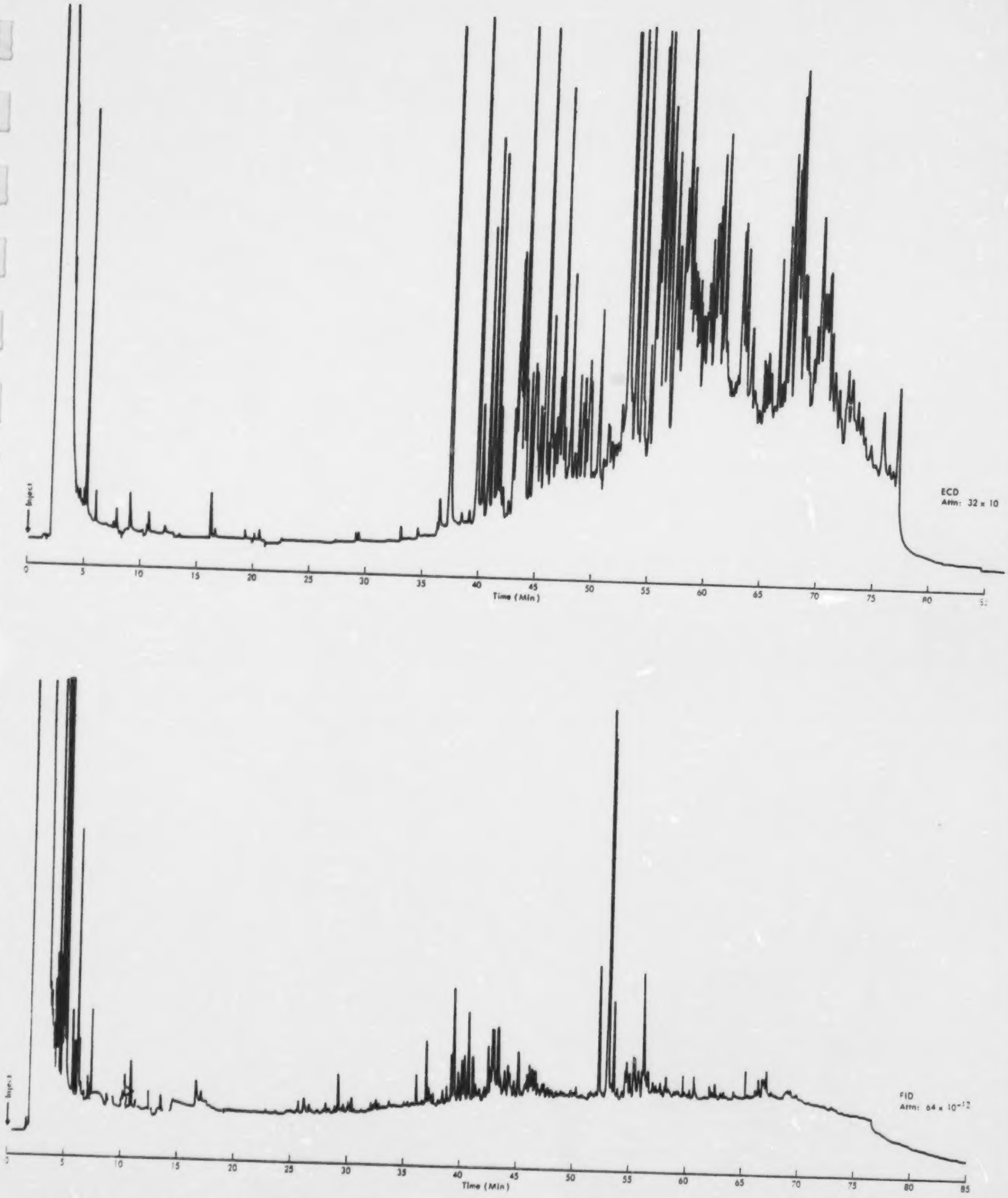

Figure 5. Capillary FID/ECD chromatogram of fraction IV obtained by silica gel cleanup/fractionation of the NBS sediment extract.

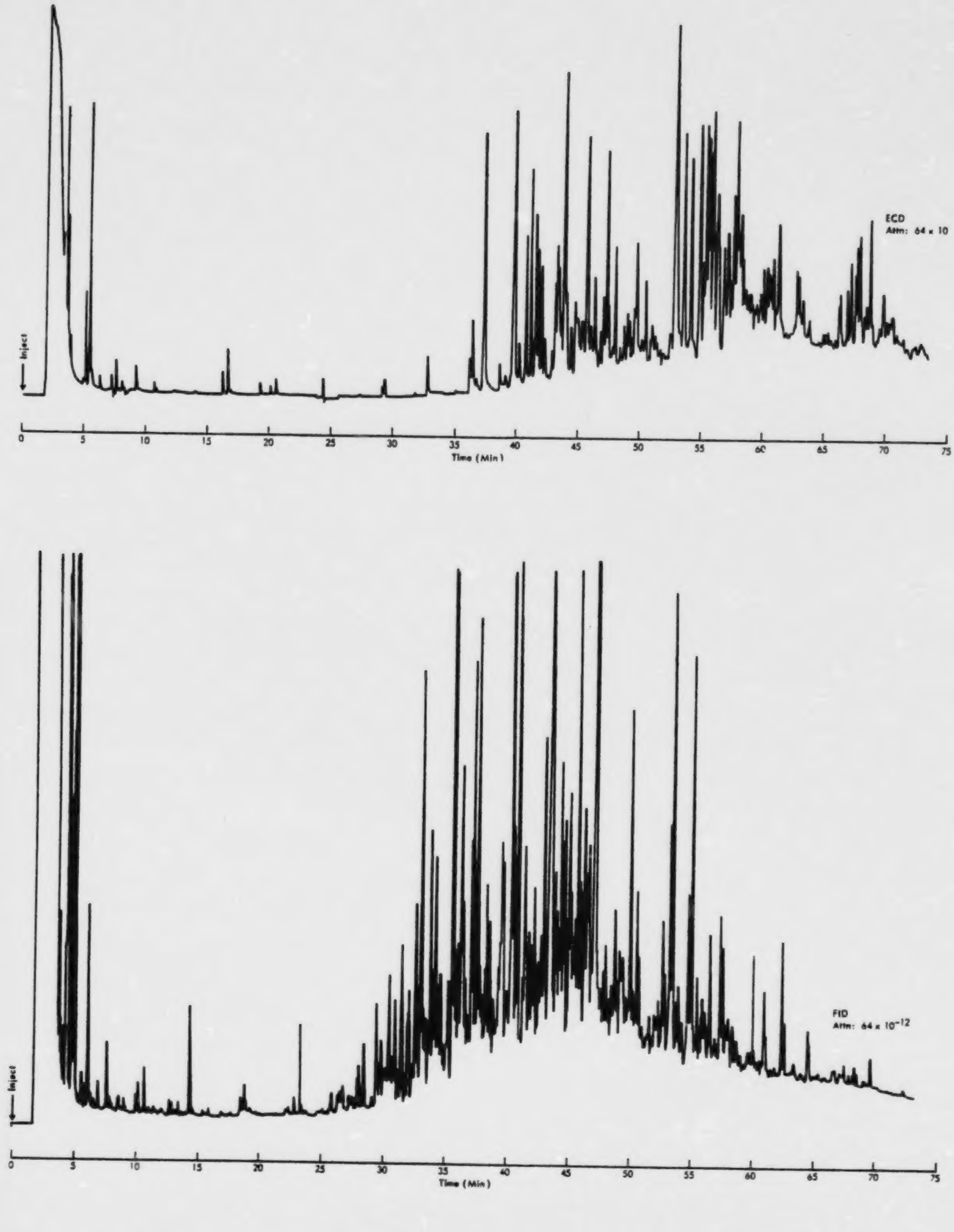

Figure 6. Capillary FID/ECD chromatogram of the combined eluent (fractions II through IV) obtained by silica gel cleanup/fractionation of the NBS sediment extract.

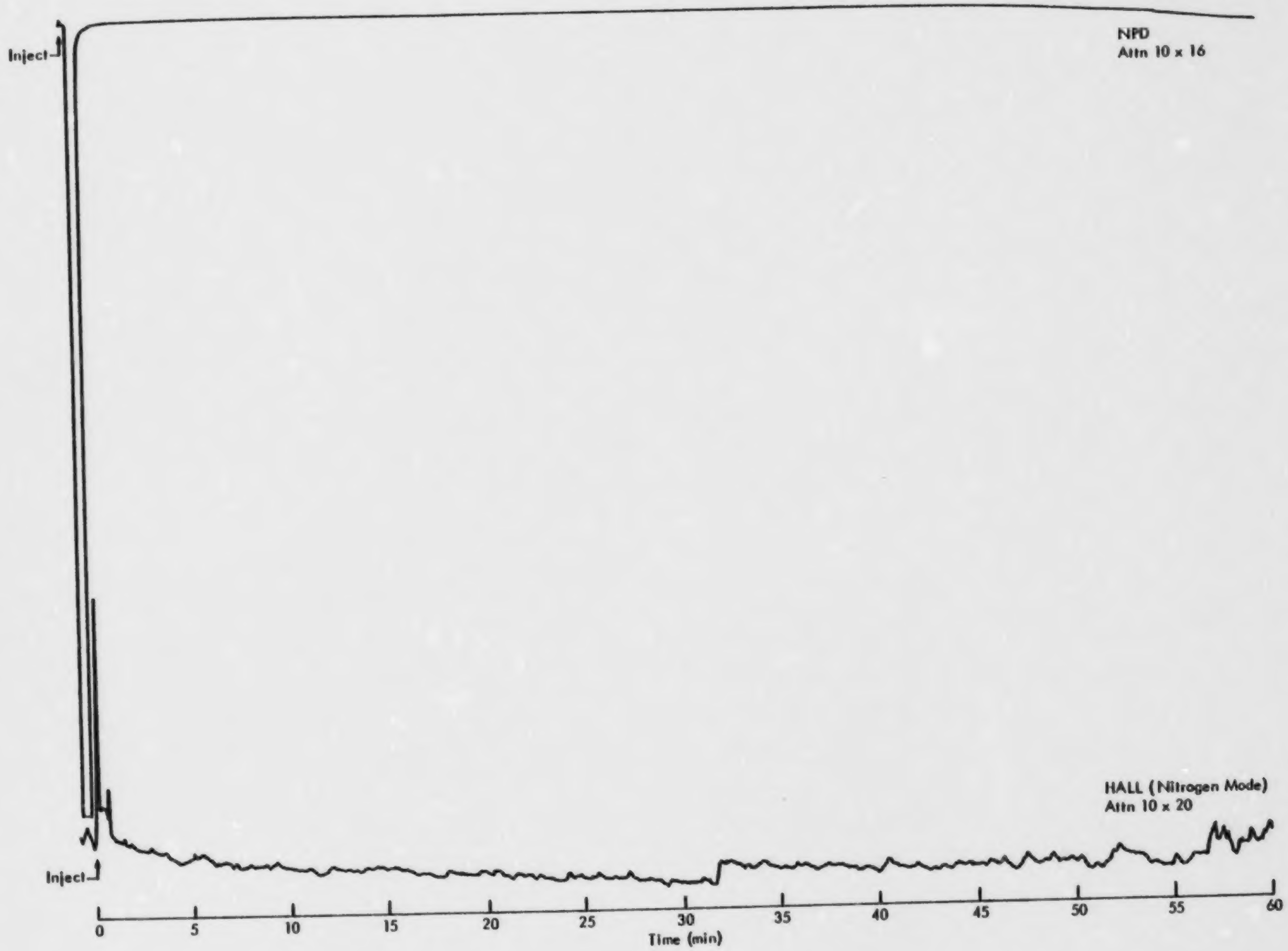

Figure 7. Capillary NPD/Hall™ chromatogram of fraction II obtained by silica gel cleanup/ fractionation of the NBS sediment extract.

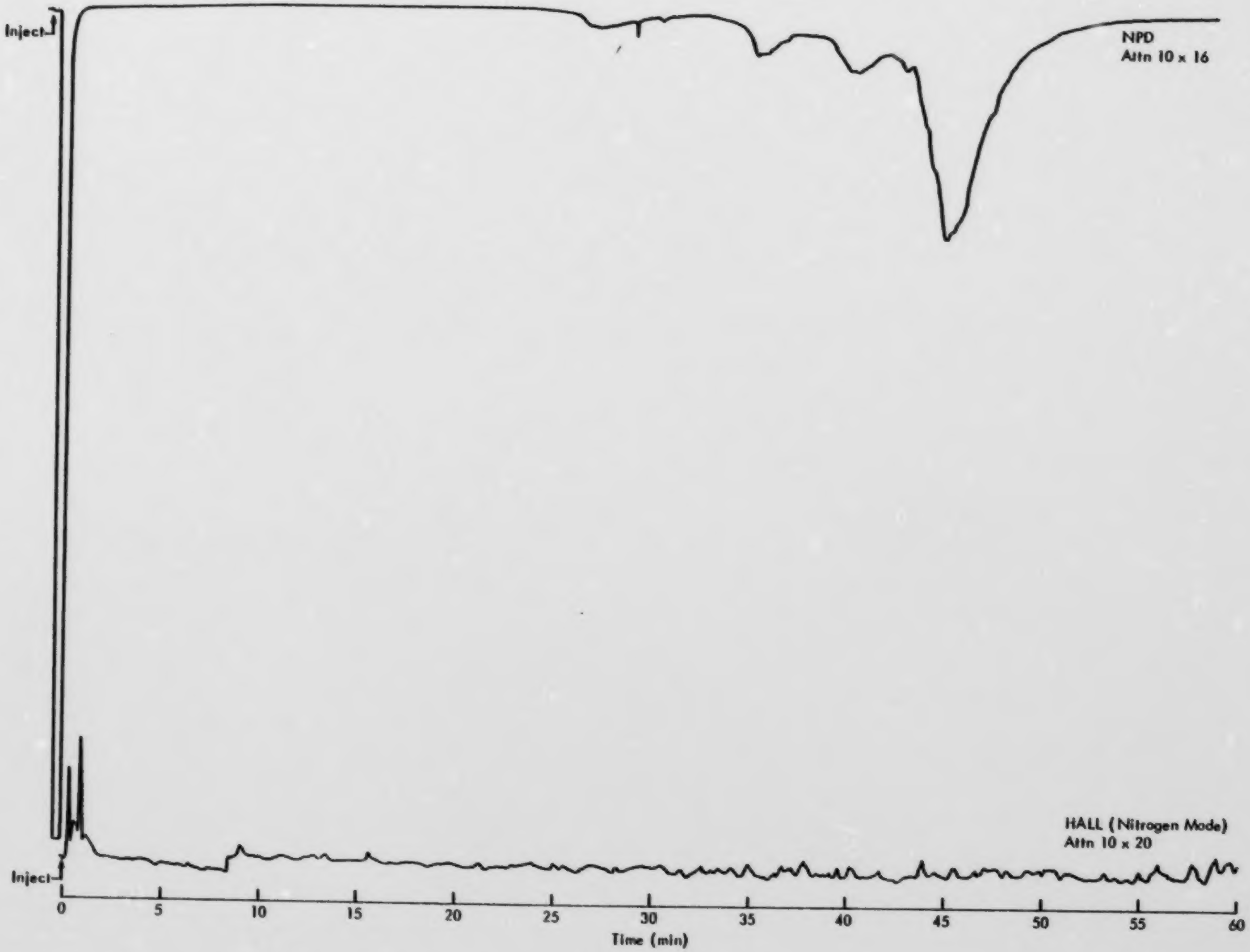

Figure 8. Capillary NPD/Hall™ chromatogram of fraction III obtained by silica gel cleanup/fractionation of the NBS sediment extract.

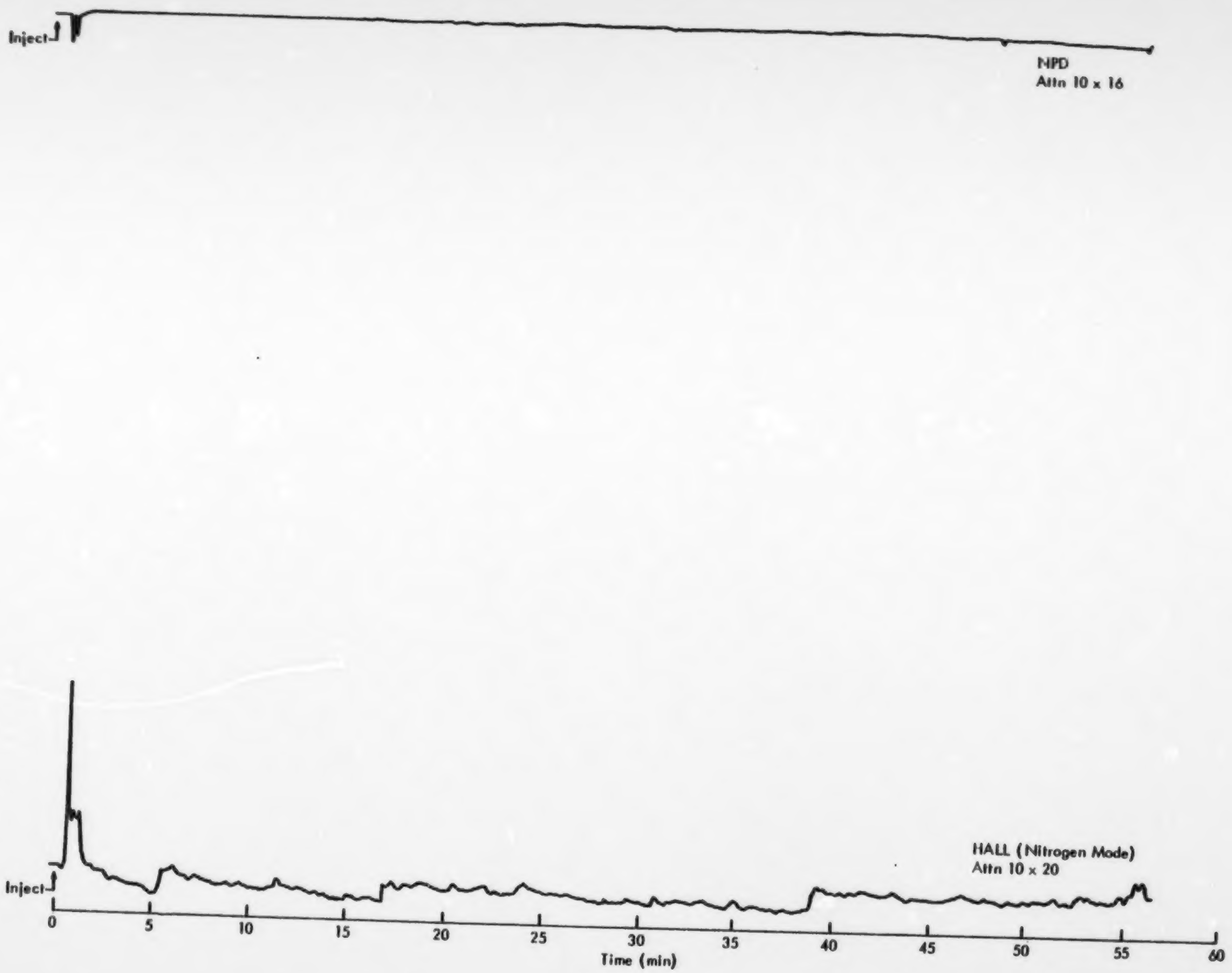

Figure 9. Capillary NPD/Hall™ chromatogram of fraction IV obtained by silica gel cleanup/fractionation.

The data presented here, although only qualitative, do provide very useful information for the analysis of the NBS sediment samples and for the identification of the sample components. First of all, it should be noted that Fraction I contains a large number of partially resolved electron-absorbing species (aromatics, halogenated aliphatics, etc.) not detected with a nonselective detector like FID. Although their identities remain unknown, their level may be estimated from the ECD chromatogram. If the analysis is done by GC/MS and their level is below the detection limit of the mass spectrometer, this information would be lost. Likewise, Fraction IV shows only few major peaks on the FID chromatogram and a very large number of peaks on the ECD chromatogram. Figures 3 and 4 indicate the level of complexity in Fractions II and III. High levels of aromatic compounds are expected to be found in these samples.

Simultaneous detection using two element-selective detectors (NPD and Hall electrolytic conductivity detector) indicated the absence of any nitrogen- and halogen-containing species in Fractions II, III, and IV. Analysis of test mixtures containing lindane, aldrin, heptachlor, and pentachloronitrobenzene indicated detection limits in the low nanogram-high picogram range when analyzed simultaneously with the gas chromatographic setup described above. The broad peak shown on the NPD chromatogram in Fraction IV may have been due to a polar compound containing nitrogen or phosphorus.

Because of the complexity of each of the fractions generated by silica gel fractionation, it was mutually decided with the sponsor to:

- Analyze Fraction I separately for all replicates of the unspiked and spiked sediment.

- Analyze Fractions II, III, and IV separately for one of the replicates of the unspiked or spiked sediment, and combine for the other two replicates.

The best compromise between the analysis time and the separation of all 42 base/neutral/pesticide compounds used in recovery studies was using the temperature program given in Table 2.

Screening of the acidic extracts with FID/ECD is shown in Figure 10. In this case the analysis time was reduced to 30 to 35 minutes by increasing the temperature programming rate to 8°C/minute.

RECOVERY STUDIES

The main objective of this task was to evaluate the sludge protocol extraction method for sediment analysis. Preliminary studies indicated that the sediment sample could be diluted with organics-free water to 25% solids on a dry weight basis, and treated as a sludge sample. Fifty-one priority pollutants (see Table 1) were selected for recovery studies. All experiments were conducted in triplicate. Recoveries were determined for each of the compounds in Table 1 at two spiking levels, namely, 400 ng/g dry sediment and 4,000 ng/g dry sediment.

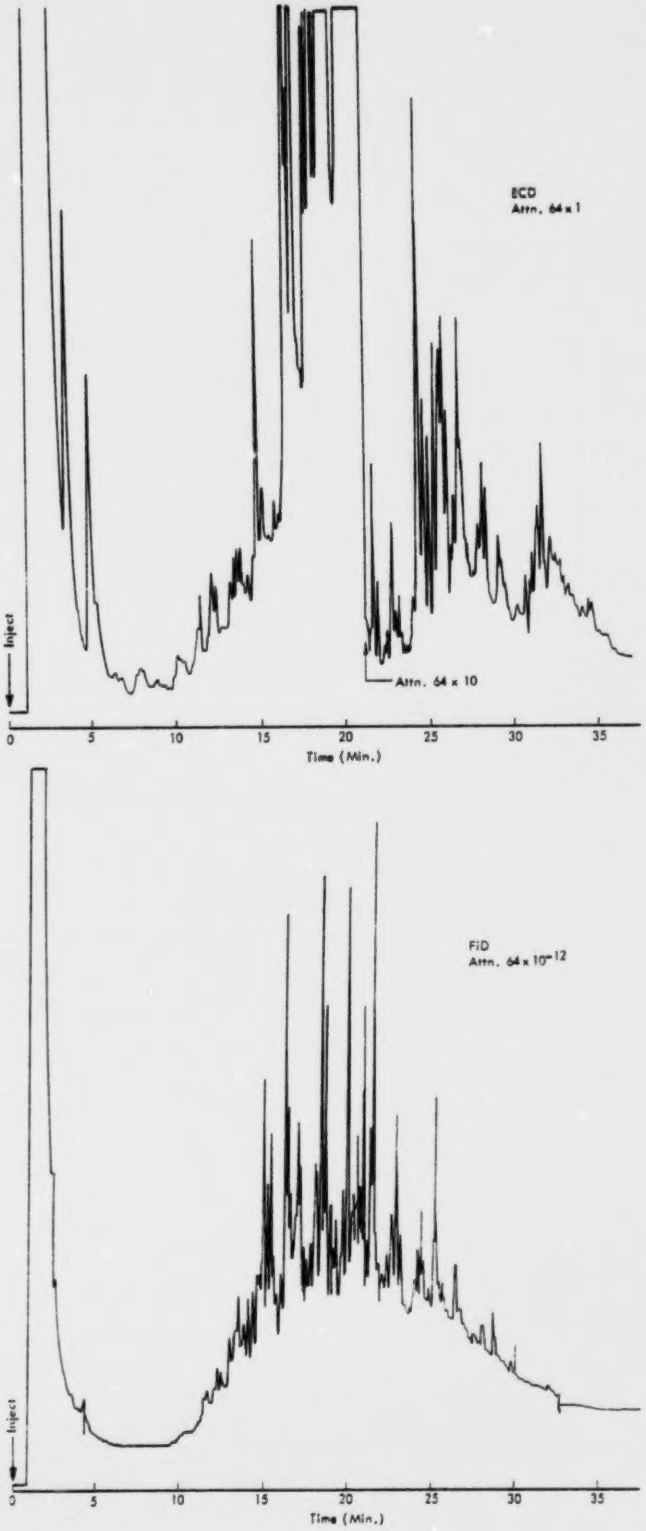

Figure 10. Capillary FID/ECD chromatogram of the acidic NBS sediment extract.

Experimental

Figure 11 shows the sample preparation and analysis scheme. A 20-g aliquot of the NBS sediment loaded in a 225-ml centrifuge bottle was diluted with 60 ml MilliQ water. The sample was homogenized with a Tekmar Tissumizer® blending probe for 30 seconds to enhance the wetting of the sediment. The spike was added immediately following homogenization and allowed to equilibrate with the sediment for 24 hours at 4°C, using a mechanical device to tumble the sample continuously. Each sample was adjusted to pH 11 with 6 N sodium hydroxide. Three sequential extractions with 80-ml aliquots of dichloromethane were performed to isolate the base/neutral compounds and the pesticides. Following each addition of dichloromethane, the sample was homogenized for 30 seconds with a Tekmar Tissumizer® blending probe, and centrifuged for 30 minutes at 2,500 revolutions per minute to promote phase separation. Three distinct layers consisting of an aqueous layer on top, a dark solvent layer in the middle, and a firm solids layer on the bottom were observed. The middle layer containing the organic compounds was removed with a 100-ml syringe, and the extraction was repeated twice. The three base/neutral/pesticide extracts were combined and dried by passage through a short column of anhydrous sodium sulfate prior to concentration to 5 ml in a Kuderna-Danish evaporator. The sediment sample was adjusted to pH 1 with 6 N hydrochloric acid, and the extraction, extract drying, and concentration steps were repeated to isolate the acidic compounds.

Triplicate unspiked samples and triplicate spiked samples (at two spike levels) were extracted by the procedure outlined above. Spike concentrations of 400 ng/g dry sediment and 4,000 ng/g dry sediment were achieved by adding 100 µl and 1,000 µl of the methanol stock solution containing 51 base/neutrals/pesticides/acids. The individual stock solutions for each compound (concentration approximately 4 mg/ml) were made in methanol except for: hexachlorobenzene, chrysene, and dibenz[a,h]anthracene stock solutions, which were made in tetrahydrofuran, and anthracene and benzo[a]pyrene stock solutions, which were made in acetone.

The base/neutral/pesticide extracts were cleaned by silica gel chromatography. Silica gel (silica Woelm, 70/150 mesh, ICN) was cleaned by a 16-hour Soxhlet extraction with dichloromethane. The solvent was allowed to evaporate in a clean hood at ambient temperature prior to activating the material at 160°C overnight. Immediately prior to use, the active silica gel was deactivated with 3% water (by weight) and was allowed to equilibrate for 4 hours with tumbling. Columns were prepared by pouring 20 g of the deactivated silica gel into a 28 cm x 2 cm ID glass column half-filled with hexane. After allowing the absorbent to settle and removing the excess solvent, the columns were rinsed with an additional 25 ml hexane.

The elution patterns and the recoveries of the 42 base/neutral/pesticide compounds from the silica gel column were determined in duplicate at two levels (8 µg and 80 µg) corresponding to the spiking levels in sediment samples. The compounds were loaded onto the silica gel column by mixing appropriate aliquots of the stock solution (100 µl for 8-µg level and 1,000 µl for 80-µg level) with 2.5 g 3% deactivated silica gel in a 10-ml beaker. The solvent was removed under a gentle stream of dry nitrogen, and the adsorbent

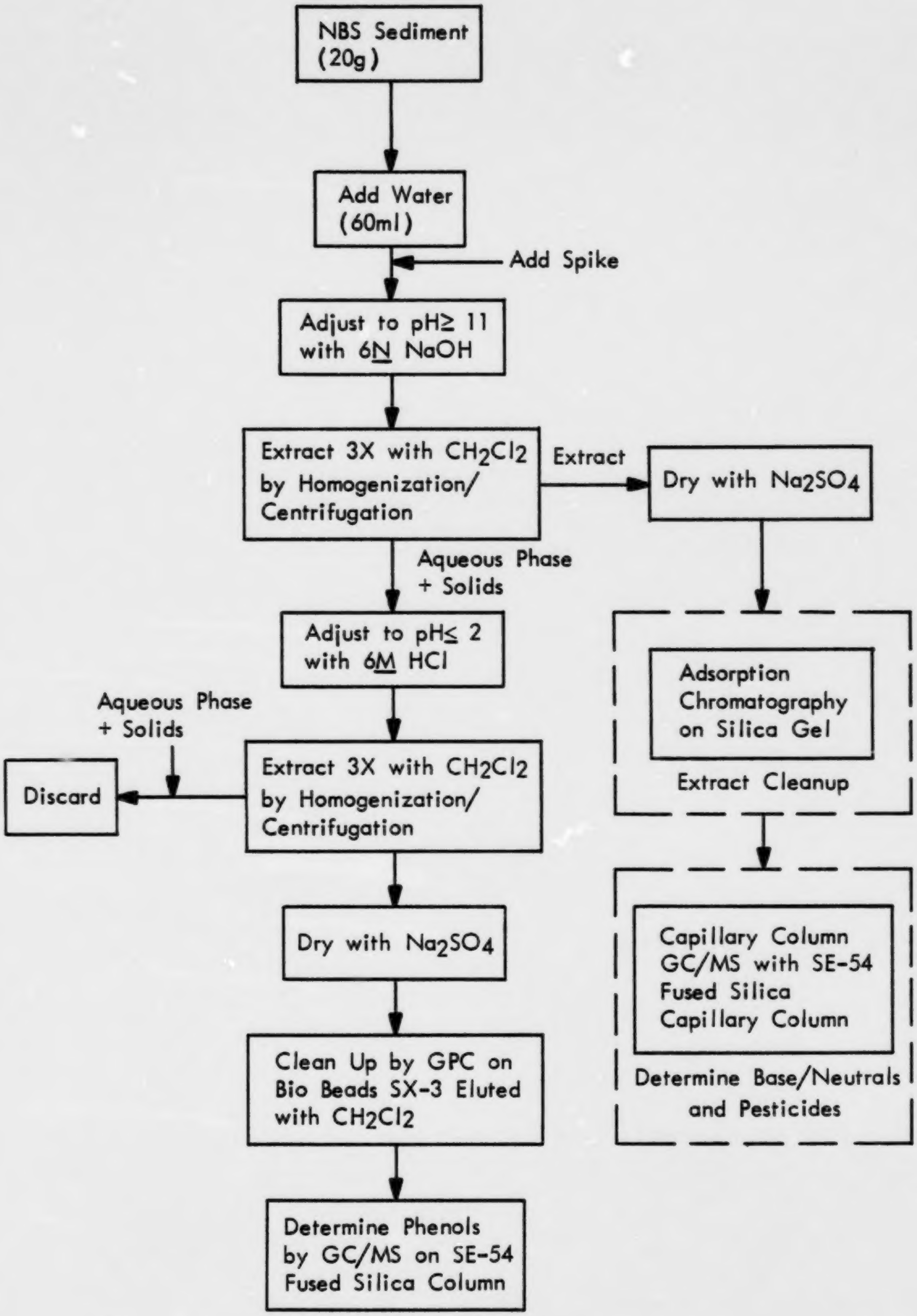
NBS Sediment (20g)
Add Water (60ml)
Add Spike
Adjust to pH≥ 11 with 6N NaOH
Extract 3X with CH_2Cl_2 by Homogenization/ Centrifugation
Extract
Dry with Na_2SO_4
Aqueous Phase + Solids
Adjust to pH≤ 2 with 6M HCl
Aqueous Phase + Solids
Discard
Extract 3X with CH_2Cl_2 by Homogenization/ Centrifugation
Dry with Na_2SO_4
Clean Up by GPC on Bio Beads SX-3 Eluted with CH_2Cl_2
Determine Phenols by GC/MS on SE-54 Fused Silica Column
Adsorption Chromatography on Silica Gel
Extract Cleanup
Capillary Column GC/MS with SE-54 Fused Silica Capillary Column
Determine Base/Neutrals and Pesticides

Figure 11. Scheme for the analysis of the NBS sediment.

containing the spikes was transferred to the top of the silica gel column for elution. The beaker was rinsed with hexane, and the rinse was added to the silica gel column. The fractions used to elute the compounds were:

Fraction I: 100 ml hexane

Fraction II: 50 ml 10% dichloromethane in hexane

Fraction III: 50 ml 50% dichloromethane in hexane

Fraction IV: 150 ml 5% acetone in dichloromethane

These fractions were collected in a Kuderna-Danish apparatus and concentrated for GC/MS analysis. The sediment extracts (5 ml) containing the base/neutral/pesticide compounds were processed identically. For one of the replicate samples Fractions I through IV were analyzed separately, whereas for the other two replicates only Fraction 1 was analyzed separately and Fractions II through IV were composited.

Extracts containing the acidic compounds were cleaned up by gel permeation chromatography. Columns were prepared from 60-g Bio-Beads SX-3 gels. The gel was soaked overnight in dichloromethane and poured into a 60 cm x 2.5 cm ID column fitted with adjustable plungers on both ends. The column was calibrated using solutions of corn oil, n-butylbenzylphthalate, and phenols (phenol, 2,4-dichlorophenol, and pentachlorophenol) following the procedures in the sludge protocol. The eluting solvent was dichloromethane at 5 ml/min. The initial 120 ml (24 minutes) of eluent was discharged. The next 150 ml (30 minutes) were collected, and 80 ml (16 minutes) were used to wash the column between runs. GPC recoveries of phenols were determined for spiked blanks at two spiking levels (8 μg and 80 μg) corresponding to the spiking levels of the sediment samples. The spiked blanks and the sediment extracts were loaded onto the column in 4-ml injections, and column elution was monitored with a 254-nm UV detector.

Table 4 lists the GC/MS conditions used. The compounds were quantitated by the internal standard method using d_8-naphthalene, d_{10}-anthracene, and d_{12}-chrysene as internal standards. Calculations were done as described in Appendix A; the compounds were grouped as follows: compounds eluting before naphthalene, including naphthalene, were quantitated using d_8-naphthalene as internal standard; compounds eluting between naphthalene and anthracene, including anthracene, were quantitated using d_{10}-anthracene as internal standard; and compounds eluting after anthracene were quantitated using d_{12}-chrysene as internal standard.

Results and Discussion

The results of the precision and accuracy determinations for the base/neutral/pesticide compounds are given in Table 5. Of all recovery determinations in Table 5, 51% fell within the range 60 to 120%. An additional 16% were below the 60% recovery, and 8% were above the 120% recovery. For almost half the compounds in Table 5, recoveries could not be determined at the lower spike level (400 ng/g) because of the high concentrations of the analytes in the unspiked sediment and standard derivations higher than the spike level.

TABLE 4. GC/MS ANALYSIS CONDITIONS

Instrument:	
Gas chromatograph:	Finnigan 9610
Mass spectrometer:	Finnigan 4023
Data system:	Incos 2300
Column:	30 m x 0.25 mm ID fused silica capillary column coated with SE-54 (J & W) routed directly into the ion source
Temperature program:	60°C (2 min) to 300°C at 4°C/min (base/neutrals/pesticides) 60°C (2 min) to 300°C at 8°C/min (acids)
Injector temperature:	275°C
Transfer line temperature:	300°C
Carrier gas:	Helium at 10 psi
Splitless injection:	30 sec
Injection volume:	2 μl
Solvent:	Dichloromethane (samples) Methanol/dichloromethane (standards)
Mass spectrometer operating conditions:	
Ion source temperature:	280°C
Ionization energy:	70 eV
Trap current:	200 μA
Electron multiplier:	-1.75 kV
Scan range:	50-450 amu
Scan speed:	1-2 sec/scan

TABLE 5. RESULTS OF THE PRECISION AND ACCURACY EVALUATIONS FOR THE SLUDGE PROTOCOL APPLIED TO THE ANALYSIS OF BASE/NEUTRAL/PESTICIDE COMPOUNDS IN THE SPIKED NBS SEDIMENT

Compound No.	Compound	Unspiked sediment[a] concentration (ng/g dry sediment)	% Recovery[a] Spike level 400 ng/g dry sediment	% Recovery[a] Spike level 4,000 ng/g dry sediment
1	Bis(2-chloroethyl) ether	ND	96 ± 23	112 ± 19
2	1,3-Dichlorobenzene	ND	63 ± 9	68 ± 16
3	1,2-Dichlorobenzene	ND	66 ± 14	75 ± 22
4	Hexachloroethane	ND	41 ± 15	62 ± 5
5	N-Nitroso-di-n-propylamine	ND	95 ± 38	89 ± 11
6	Nitrobenzene	ND	43 ± 3	102 ± 26
7	Bis(2-chloroethoxy)methane	ND	94 ± 39	81 ± 11
8	1,2,4-Trichlorobenzene	ND	67 ± 4	58 ± 13
9	Naphthalene	880 ± 350	64[c]	70 ± 35
10	Hexachlorobutadiene	ND	63 ± 2	71 ± 17
11	Hexachlorocyclopentadiene	ND	0	0
12	2-Chloronaphthalene	ND	72 ± 10	94 ± 20
13	Acenaphthylene	1,820 ± 350	d	86 ± 24
14	2,6-Dinitrotoluene	ND	110 ± 51	102 ± 36
15	Acenaphthene	850 ± 120	d	104 ± 24
16	2,4-Dinitrotoluene	ND	49[c]	64 ± 50
17	Fluorene	1,580 ± 130	d	82 ± 7
18	4-Chlorophenyl phenyl ether	ND	86 ± 42	74 ± 7
19	Diethylphthalate	ND	33 ± 14	109 ± 13
20	4-Bromophenyl phenyl ether	ND	91 ± 50	89 ± 2
21	Hexachlorobenzene	ND	46 ± 10	53 ± 4
22	Phenanthrene	3,770 ± 300	d	83 ± 26
23	Anthracene	2,090 ± 72	d	25 ± 11
24	Di-n-butylphthalate	580 ± 65	156[c]	100, 137
25	Fluoranthene	14,760 ± 2,810	d	174 ± 78
26	Pyrene	20,020 ± 4,630	d	148, 252
27	Benzidine[b]	ND	0	0
28	Endosulfan sulfate	1,160, 455	97, 137	0

(continued)

TABLE 5 (continued)

Compound No.	Compound	Unspiked sediment[a] concentration (ng/g dry sediment)	% Recovery[a] Spike level 400 ng/g dry sediment	% Recovery[a] Spike level 4,000 ng/g dry sediment
29	n-Butylbenzylphthalate	920	d	103[c]
30	Chrysene	27,000 ± 6,500	d	d
31	3,3'-Dichlorobenzidine	ND	0	0
32	Bis(2-ethylhexyl)phthalate	7,560, 10,790	d	d
33	Benzo[a]pyrene	22,850 ± 6,200	d	128 ± 23
34	Dibenzo[a,h]anthracene	5,960 ± 420	d	113 ± 42
35	γ-BHC	3,050 ± 1,270	d	50 ± 19
36	Aldrin	ND	44[c]	22 ± 13
37	Heptachlorepoxide	ND	0	54 ± 9
38	p,p'-DDE	340 ± 100	41[c]	76 ± 32
39	Endrin	ND	0	0
40	p,p'-DDD	120	121, 186	104 ± 18
41	p,p'-DDT	840 ± 20	d	155 ± 43
42	α-Endosulfan	ND	0	0

ND = Not detected.

[a] Mean ± standard deviation for three determinations.

[b] Benzidine not detected by GC/MS in any of the standards at concentrations ≦ 80 ng/μl.

[c] Single determination reported; levels in the other replicates were below the unspiked sediment level.

[d] Concentrations determined in the spiked sediment were below the unspiked sediment level.

For example, fluoranthene, pyrene, chrysene, and benzo[a]pyrene had levels above 10,000 ng/g dry sediment. Furthermore, because of the complexity of the sediment sample, coeluting compounds may have also accounted for the high standard deviations of the recoveries of many of the spikes and the very poor recoveries of several compounds in Table 5. Zero recoveries were found at both spike levels for the following compounds: hexachlorocyclopentadiene, benzidine, 3,3'-dichlorobenzidine, heptachlorepoxide (only at 400 ng/g dry sediment), endrin, and α-endosulfan. This was expected for benzidine, which could not be detected by GC/MS in any of the standards at levels ≦ 20 ng/μl. The other base/neutral/pesticide compounds, however, had recoveries > 40% when spiked blanks were fractionated by silica gel chromatography (see Tables 6 and 7).

Tables 6 and 7 give the elution patterns and the recoveries of base/neutral/pesticide compounds from spiked blanks by silica gel chromatography at 8 μg and 80 μg total spike, respectively. It can be noted that most of the halogenated hydrocarbons (dichlorobenzenes, trichlorobenzene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachlorobenzene) elute in the hexane fraction (FI), whereas the polycyclic aromatic hydrocarbons (fluoranthene, pyrene, benzo[a]pyrene, dibenzo[a,h]anthracene) elute in fraction FIII. The more polar compounds such as bis(2-chloroethyl) ether, N-nitroso-di-n-propylamine, bis(2-chloroethoxy)methane, dinitrotoluenes, and phthalates were identified in fraction FIV. Several compounds (naphthalene, chloronaphthalene, γ-BHC, and p,p'-DDE) were found in two or three of the silica gel fractions.

Data in Tables 6 and 7 also indicate that with two or three exceptions the recoveries of the base/neutral/pesticide compounds are quantitative and reproducible. The poor chromatographic behavior of hexachlorobutadiene and hexachlorocyclopentadiene resulted in the excessively high recovery values given in Tables 6 and 7.

The results of the precision and accuracy determinations for the acidic compounds are given in Table 8. Of all recovery determinations, 61% were greater than 63%, 11% were between 40% and 60%, and 28% were zero. High recoveries (> 70%) were found at both spike levels for phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, and pentachlorophenol. Zero recoveries were found for 2,4-dinitrophenol and 2,4-dinitrocresol at both spike levels, and 4-nitrophenol at the lower spike level. This was in part expected since, as the recovery data of phenols from spiked blanks by GPC (Table 9) indicate, the dinitrophenols could not be recovered from spiked blanks at the lower spike level. However, they were quantitatively recovered from spiked blanks at the higher spike level. Coeluting interferences may have obscured these compounds, or because of their polar nature and their relatively high water solubilities they may not have been recovered by extraction with methylene chloride. 4-Nitrophenol was only poorly recovered at the higher spike level.

Given the complexity of the matrix, the precision and accuracy results presented here demonstrate that the sludge protocol can be applied with minor modifications to the analysis of sediments. Although the evaluation experiments were conducted using a set of priority pollutants, representative of all of the EPA's priority pollutants, it may also be useful for many of the nonpriority pollutants.

TABLE 6. RECOVERIES OF BASE/NEUTRAL/PESTICIDE COMPOUNDS FROM SPIKED BLANKS BY SILICA GEL CHROMATOGRAPHY[a]

Compound No.	Compound	% Recovery in fraction[b] 100% Hexane (FI) (100 ml)	10% Methylene chloride in hexane (FII) (50 ml)	50% Methylene chloride in hexane (FIII) (50 ml)	5% Acetone in methylene chloride (FIV) (150 ml)	Total recovery
1	Bis(2-chloroethyl) ether				97 , 125	97, 125
2	1,3-Dichlorobenzene	70 , 56				70, 56
3	1,2-Dichlorobenzene	76 , 56				76, 56
4	Hexachloroethane	77 , 55				77, 55
5	N-Nitroso-di-n-propylamine				94 , 103	94, 103
6	Nitrobenzene			6.3, 1.1	60 , 70	66, 71
7	Bis(2-chloroethoxy)methane				59 , 69	59, 69
8	1,2,4-Trichlorobenzene	62 , 49				62, 49
9	Naphthalene	18 , 7.1	14 , 45	17 , 2.9		49, 55
10	Hexachlorobutadiene	193 , 178				193, 178
11	Hexachlorocyclopentadiene	344 , 344				344, 344
12	2-Chloronaphthalene	61 , 61	26 , 34			87, 95
13	Acenaphthylene	2.4, ND	2.8, 37	97 , 50		102, 87
14	2,6-Dinitrotoluene				66 , 107	66, 107
15	Acenaphthene		4.9, 56	70 , 33		75, 89
16	2,4-Dinitrotoluene				74 , 98	74, 98
17	Fluorene			96 , 114		96, 114
18	4-Chlorophenyl phenyl ether			95 , 125		95, 125
19	Diethylphthalate				111 , 139	111, 139
20	4-Bromophenyl phenyl ether			104 , 138		104, 138
21	Hexachlorobenzene	163 , 158				163, 158
22	Phenanthrene		1.4, 3.8	98 , 117		99, 121
23	Anthracene		2.1, 8.1	96 , 107		98, 115
24	Di-n-butylphthalate				108 , 138	108, 138
25	Fluoranthene			74 , 25		74, 25
26	Pyrene		0.8, 2.1	68 , 75		69, 77
27	Benzidine[c]					-
28	Endosulfan sulfate				42 , 80	42, 80
29	n-Butylbenzylphthalate			1.9, ND	65 , 140	67, 140
30	Chrysene			72 , 78		72, 78
31	3,3'-Dichlorobenzidine[c]					
32	Bis(2-ethylhexyl)phthalate		3.0, 2.6	5.1, ND	76 , 181	84, 183
33	Benzo[a]pyrene			95 , 81		95, 81
34	Dibenzo[a,h]anthracene			106 , 68		106, 68
35	γ-BHC			26 , 27	34 , 4.1	60, 31
36	Aldrin	78 , 61	4.9, 8.3		1.8, 2.1	85, 71
37	Heptachlor epoxide			28 , 50	63 , 39	91, 89
38	p,p'-DDE	51 , 35	16 , 34	12 , 5.1		79, 74
39	Endrin				ND , ND	ND, 100
40	p,p'-DDD		0.4, 2.9	72 , 70		72, 73
41	p,p'-DDT		1.8, 33	83 , 24	5.9, 11	91, 68
42	α-Endosulfan			14 , ND	82 , 99	196, 99

[a] Silica gel extracted for 24 hr with methylene chloride, activated for 24 hr at 160°C, and deactivated with water (3% by weight).

[b] Total spike 8 μg for each compound.

[c] Not detected by GC/MS in any of the silica gel fractions.

TABLE 7. RECOVERIES OF BASE/NEUTRAL/PESTICIDE COMPOUNDS FROM SPIKED BLANKS BY SILICA GEL CHROMATOGRAPHY[a]

Compound No.	Compound	% Recovery[b] in fraction: 100% Hexane (FI) (100 ml)	10% Methylene chloride in hexane (FII) (50 ml)	50% Methylene chloride in hexane (FIII) (50 ml)	5% Acetone in methylene chloride (FIV) (150 ml)	Total recovery
1	Bis(2-chloroethyl) ether				79 , 77	79, 77
2	1,3-Dichlorobenzene	68 , 61				68, 61
3	1,2-Dichlorobenzene	71 , 64				71, 64
4	Hexachloroethane	88 , 71				88, 71
5	N-Nitroso-di-n-propylamine				100 , 77	100, 77
6	Nitrobenzene			10 , 3.2	59 , 60	69, 63
7	Bis(2-chloroethoxy)methane				68 , 67	68, 67
8	1,2,4-Trichlorobenzene	85 , 82				85, 82
9	Naphthalene	0.2, 3.2	40 , 32	20 , 31		60, 66
10	Hexachlorobutadiene	115 , 85				115, 85
11	Hexachlorocyclopentadiene	283 , 229				283, 229
12	2-Chloronaphthalene	34 , 50	61 , 50			95, 100
13	Acenaphthylene		18 , 0.6	45 , 55		63, 56
14	2,6-Dinitrotoluene				104 , 96	104, 96
15	Acenaphthene		51 , 5.4	53 , 77		104, 83
16	2,4-Dinitrotoluene				103 , 106	103, 106
17	Fluorene			62 , 71	3.2, 0.7	65, 72
18	4-Chlorophenyl phenyl ether			105 , 110		105, 110
19	Diethylphthalate				56 , 56	56, 56
20	4-Bromophenyl phenyl ether			108 , 114		108, 114
21	Hexachlorobenzene	111 , 114				111, 114
22	Phenanthrene			55 , 62	2.8, 0.7	58, 63
23	Anthracene			55 , 61	2.5, 0.7	58, 62
24	Di-n-butylphthalate				41 , 33	41, 33
25	Fluoranthene			50 , 52	2.6, 0.8	53, 53
26	Pyrene			50 , 52	2.0, 0.4	52, 52
27	Benzidine[c]					-
28	Endosulfan sulfate				76 , 69	76, 69
29	n-Butylbenzylphthalate				75 , 67	75, 67
30	Chrysene			65 , 67	2.2, 2.5	67, 69
31	3,3'-Dichlorobenzidine				38 , 41	38, 41
32	Bis(2-ethylhexyl)phthalate				61 , 50	61, 50
33	Benzo[a]pyrene			18 , 81	1.6, 2.5	20, 83
34	Dibenzo[a,h]anthracene			84 , 66	2.0, 9	86, 75
35	γ-BHC	5.1, 4.4	5.7	78 , 54	7.6, 18	91, 82
36	Aldrin	54 , 50	4.0, 2.5			58, 53
37	Heptachlor epoxide			53 , 24	34 , 59	87, 83
38	p,p'-DDE	2.3, 17	73 , 42	14 , 20		89, 79
39	Endrin				ND , 46	ND, 46
40	p,p'-DDD			86 , 77	1.8, 2.5	88, 79
41	p,p'-DDT			80 , 94	16 , 14	96, 108
42	α-Endosulfan			31 , ND	57 , 61	88, 61

[a] Silica gel extracted for 24 hr with methylene chloride, activated for 24 hr at 160°C, and deactivated with water (3% by weight).

[b] Total spike 80 μg for each compound.

[c] Benzidine not detected by GC/MS in any of the silica gel fractions.

TABLE 8. RESULTS OF THE PRECISION AND ACCURACY EVALUATIONS FOR THE SLUDGE PROTOCOL APPLIED TO THE ANALYSIS OF ACIDIC COMPOUNDS IN THE SPIKED NBS SEDIMENT

Compound No.	Compound	Unspiked sediment concentration (ng/g dry sediment)	% Recovery	
			Spike level 400 ng/g dry sediment	Spike level 4,000 ng/g dry sediment
1	Phenol	1,810, 2,005	112, 128	78 ± 21
2	2-Chlorophenol	ND	106 ± 11	78 ± 18
3	2,4-Dimethylphenol	ND	99 ± 12	55 ± 3
4	2,4-Dichlorophenol	ND	99 ± 16	76 ± 5
5	2,4,6-Trichlorophenol	ND	67 ± 8	63 ± 10
6	2,4-Dinitrophenol	ND	0	0
7	4-Nitrophenol	ND	0	46 ± 11
8	4,6-Dinitrocresol	ND	0	0
9	Pentachlorophenol	ND	95 ± 2	71 ± 3

TABLE 9. RECOVERIES OF PHENOLS FROM SPIKED BLANKS BY GEL PERMEATION CHROMATOGRAPHY

Compound No.	Compound	% Recovery[a] 8 μg on column	% Recovery[a] 80 μg on column
1	Phenol	66	79
2	2-Chlorophenol	67	82
3	2,4-Dimethylphenol	59	69
4	2,4-Dichlorophenol	56	79
5	2,4,6-Trichlorophenol	72	86
6	2,4-Dinitrophenol	0	112
7	4-Nitrophenol	45	91
8	4,6-Dinitro-*o*-cresol	0	126
9	Pentachlorophenol	42	86

[a] Single measurement.

In fact, the qualitative information presented in Section 6 indicates that a large number of polycyclic aromatic hydrocarbons and sulfur-containing heterocyclics were isolated from the sediment matrix by the extraction procedure described above.

Fractionation of the sediment extract containing the base/neutral/pesticide compounds by silica gel chromatography helped reduce the sample complexity, thus improving the quantitation of the priority pollutants without any significant effect on the analyte recovery.

Despite efforts to clean the acidic POTW sludge extracts by gel permeation chromatography and cesium silicate chromatography, acidic compounds in POTW sludges could not be analyzed using fused silica capillary columns. Analysis of the NBS sediment extracts containing the acidic compounds was successfully performed using a fused silica capillary column coated with SE-54. The inertness and excellent resolution of the capillary column allowed the detection of nanogram levels (1 ng/µl) of phenols in the presence of high levels of interfering coextractants.

CHROMATOGRAPHIC QUALITY ASSURANCE

The emphasis of this task was on the quantitation of the 51 priority pollutant compounds used for recovery studies and on the identification of all organic compounds in the NBS sediment extract. Consequently, the reliability of the quantitative and qualitative information depends ultimately upon the chromatographic procedures of silica gel cleanup/fractionation, gel permeation chromatography, and gas chromatography using fused silica capillary columns.

The quality assurance standards used in cleanup/fractionation procedures were discussed in the recovery section. This section addresses the procedures used to assure proper performance of the GC/MS instrumentation.

Column Performance

Following the installation of the capillary column into the GC/MS system, a standard test mixture containing 20 ng each of 2,6-dimethylphenol, 2,6-dimethylaniline, 1-octanol, 2-octanone, *n*-tridecane, *n*-tetradecane, and *n*-pentadecane was analyzed to determine the number of effective plates (N_{eff}), peak asymmetry, column pH, separation number, and column adsorptivity. Each of the above-mentioned parameters was found to satisfy the acceptance criteria given in Appendix A. Every day, at the beginning of the day and sometimes late in the day, a set of standards containing the 42 base/neutral/pesticide compounds and the 9 acidic compounds at 5 ng/µl and 20 ng/µl was analyzed with each set of samples. The acceptance criteria were coincidence of the retention times and less than 10% relative deviation in the reproducibility of the response factors for most of the components in the two standard test mixtures.

Three internal standards, d_8-naphthalene, d_{10}-anthracene, and d_{12}-chrysene, were added to each sample prior to GC/MS analysis. In selecting these internal standards, consideration was given to: (a) the unlikeliness of the internal standard being in the sample matrix; (b) chromatographic resolution between compounds of interest and the internal standards; and (c) the need to cover the wide range of volatilities of components in the sample. d_8-Naphthalene and naphthalene should be resolved (30% valley), phenanthrene and anthracene should be well-resolved, and d_{10}-anthracene should elute between them. Chrysene and d_{12}-chrysene should also be resolved. Chromatograms of the base/neutral/pesticide standard and phenol standard are shown in Figures 12 and 13. Exemplification of the reproducibility of retention times and relative response factors (RRF) determined on the same day with a 4-hour interval between GC/MS runs is shown in Table 10. The reproducibility of retention time is excellent; the largest difference was found to be five scans. The percent relative deviation of the RRF for most compounds was less than 10%; however, several compounds exhibited relative deviations between 10 and 20%. All the relative retention times (RRT) and RRFs were calculated using the internal standard that eluted closest to the analyte of interest. Tables 11 and 12 summarize the RRTs and RRFs used in calculations.

Mass Spectrometer Tuning

Decafluorotriphenylphosphine (DFTPP) was used to calibrate the mass spectrometer, according to Eichelberger's criteria.[3]

GC/MS Transfer Line

A comparison of the absolute peak counts obtained with the capillary column connected to the ion source with a transfer line and routed directly without any transfer line is given in Table 13. Data indicate a two- to threefold increase in sensitivity for the late eluting compounds when the capillary column is routed directly into the ion source. Several compounds (endosulfan sulfate, 3,3'-dichlorobenzidine, and endrin) which were not detected at 10-ng injections perhaps due to adsorptive sites in the transfer line could thus be detected. All GC/MS analyses were conducted with the fused silica capillary column routed into the ion source.

DOUBLE PEAKING

During the course of the experiments a serious problem with double peaking was encountered. Although it is beyond the purpose of this task to determine how to avoid this phenomenon, two solutions are recommended:

1. Change from splitless injection to on-column injection, with injection volumes of 0.2 to 0.5 µl.

2. Use fused silica capillary columns of higher capacity (0.25 to 1 µ film thicknesses).

These recommendations are based on the results of the recovery studies and of a few preliminary experiments undertaken to determine the cause of this problem.

The double peaking phenomenon was not observed when standards containing the base/neutral/pesticide compounds (shown in Table 1) were chromatographed on the fused silica capillary column (see Figures 14 through 16) and occurred only in the sample extracts, specifically in the midregion of the chromatogram, where the most concentrated sample components were eluting. This phenomenon was not observed for the early eluting (d_8-naphthalene) or the late eluting (d_{12}-chrysene) internal standards (Figures 17 and 18).

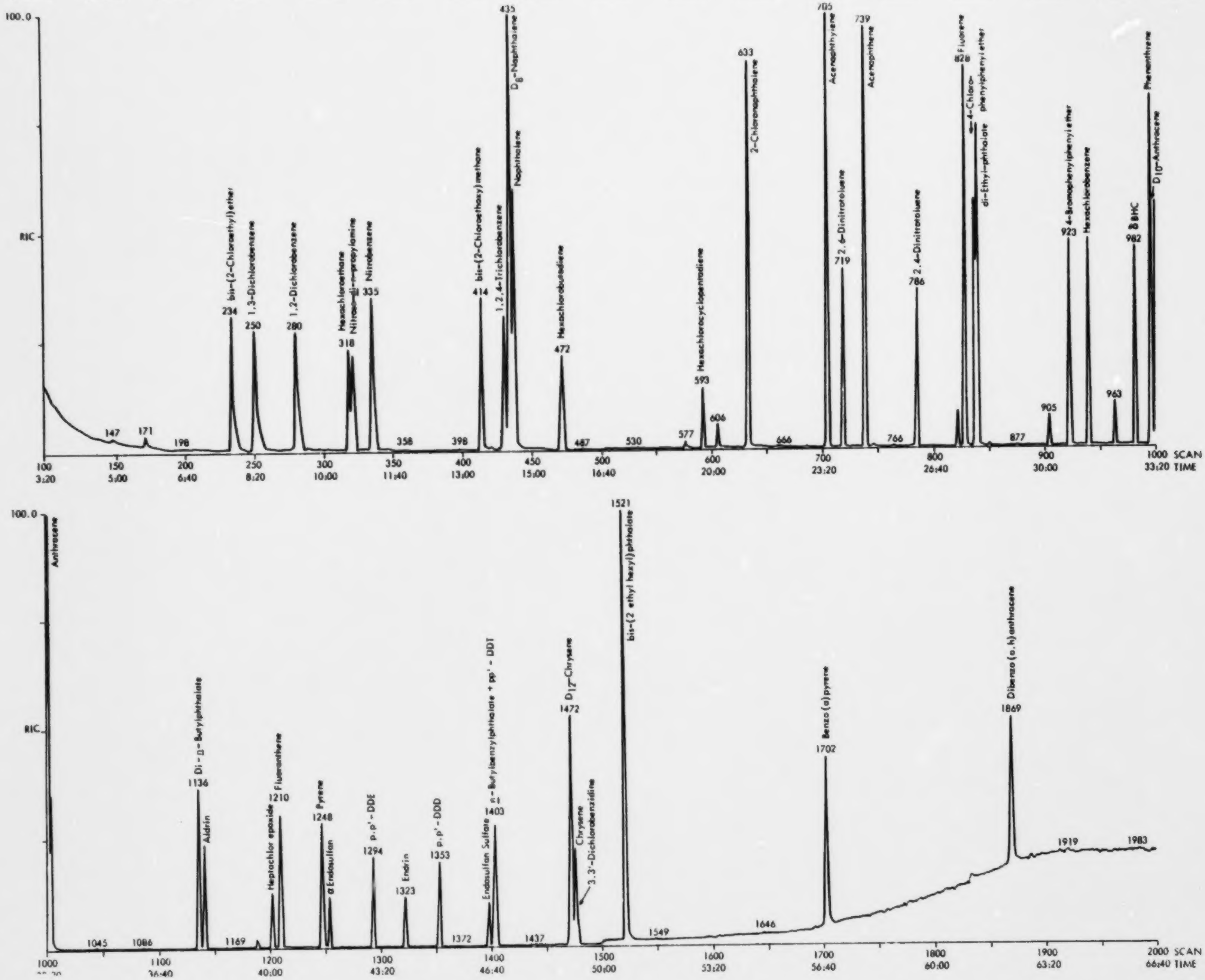

Figure 12. Capillary GC/MS chromatogram of base/neutral/pesticide test compounds.

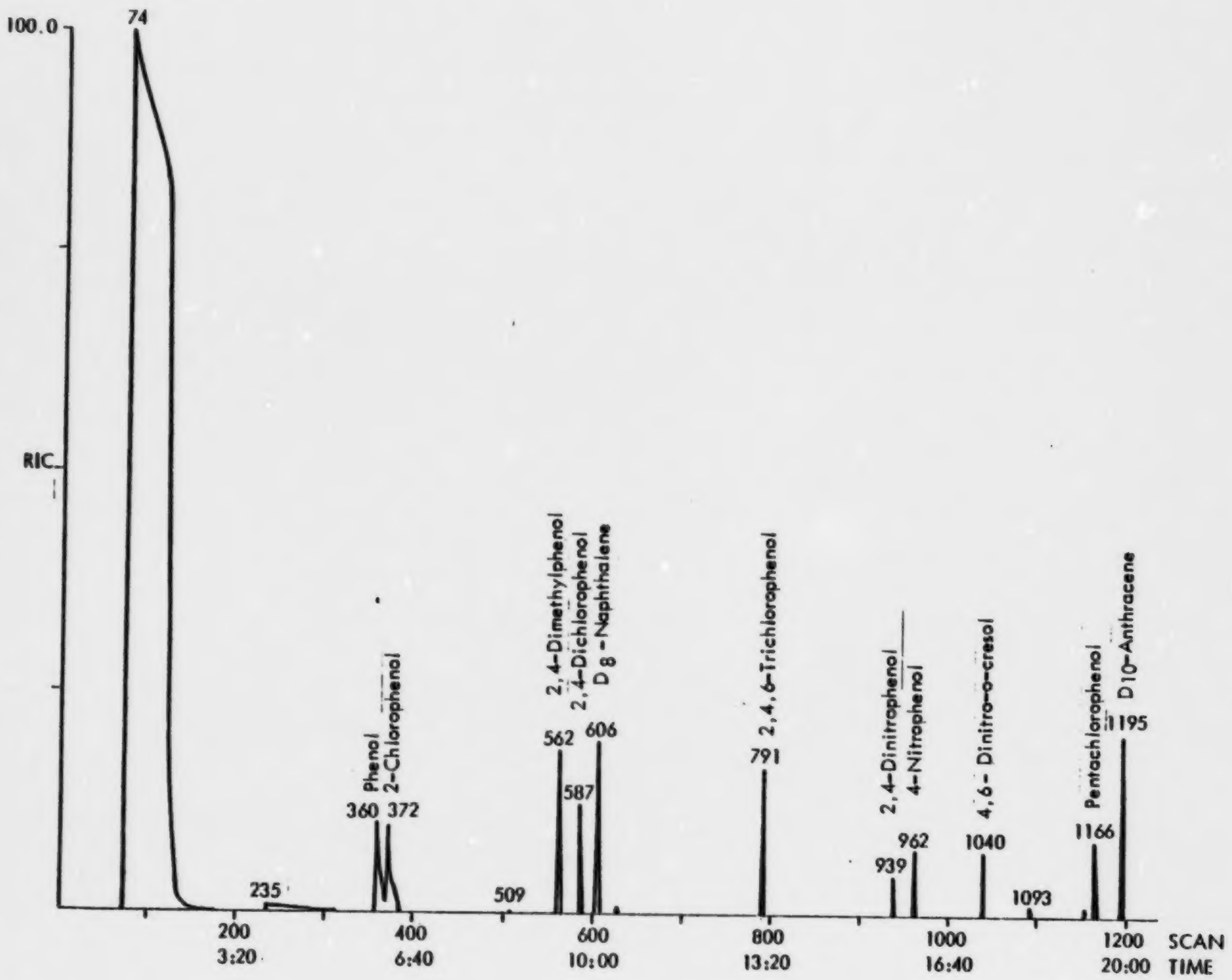

Figure 13. Capillary GC/MS chromatogram of the acidic test compounds.

TABLE 10. REPRODUCIBILITY OF THE RETENTION TIME (SCAN NUMBER) AND THE RELATIVE RESPONSE FACTORS

Compound No.	Compound	Scan No.		Relative response factor (RRF)[a]		% Relative deviation
		2/5/81 at 11:15 AM	2/5/81 at 13:24 PM	2/5/81 at 11:15 AM	2/5/81 at 13:24 PM	
1	Bis(2-chloroethyl) ether	240	b	0.486	b	
2	1,3-Dichlorobenzene	255	b	0.458	b	
3	1,2-Dichlorobenzene	284	b	0.383	b	
4	Hexachloroethane	321	b	0.275	b	
5	N-Nitroso-di-n-propylamine	325	b	0.069	b	
6	Nitrobenzene	340	b	0.474	b	
7	Bis(2-chloroethoxy)methane	417	b	0.671	b	
8	1,2,4-Trichlorobenzene	432	427	0.413	0.416	0.5
9	Naphthalene	439	434	1.823	1.790	1.3
IS	d_8-Naphthalene	436	431	1.000	1.000	-
10	Hexachlorobutadiene	473	468	0.306	0.247	15.1
11	Hexachlorocyclopentadiene	594	589	0.094	0.084	7.9
12	2-Chloronaphthalene	635	631	0.710	0.610	10.7
13	Acenaphthylene	706	702	1.450	1.503	2.5
14	2,6-Dinitrotoluene	723	720	0.155	0.143	5.7
15	Acenaphthene	740	736	1.075	1.060	1.0
16	2,4-Dinitrotoluene	792	789	0.182	0.147	15.0
17	Fluorene	830	827	1.156	1.065	5.8
18	4-Chlorophenyl phenyl ether	840	838	0.339	0.348	1.8
19	Diethylphthalate	843	840	1.306	1.258	2.6
20	4-Bromophenyl phenyl ether	925	923	0.243	0.204	12.3
21	Hexachlorobenzene	942	940	0.294	0.274	5.0
22	Phenanthrene	999	996	1.485	1.407	3.8
23	Anthracene	1007	1004	1.296	1.228	3.8
IS	d_{10}-Anthracene	1004	1002	1.000	1.000	-
24	Di-n-butylphthalate	1140	1139	4.806	4.210	9.3
25	Fluoranthene	1213	1212	2.680	2.230	13.0
26	Pyrene	1251	1249	2.192	2.068	4.1
27	Benzidine[c]	-	-	ND	ND	-

(continued)

TABLE 10 (continued)

Compound No.	Compound	Scan No. 2/5/81 at 11:15 AM	Scan No. 2/5/81 at 13:24 PM	Relative response factor (RRF)[a] 2/5/81 at 11:15 AM	Relative response factor (RRF)[a] 2/5/81 at 13:24 PM	% Relative deviation
28	Endosulfan sulfate	1402	1406	0.138	0.136	1.0
29	*n*-Butylbenzylphthalate	1407		0.670	0.599	7.9
30	Chrysene	1480	1478	1.476	1.374	5.1
31	3,3'-Dichlorobenzidine	1486	1483	0.063	0.056	8.2
32	Bis(2-ethylhexyl)phthalate	1525	1524	1.084	0.832	18.6
33	Benzo[*a*]pyrene	1707	1704	0.860	0.869	0.7
34	Dibenzo[*a*,*h*]anthracene	1875	1871	0.523	0.598	9.5
35	γ-BHC	985	983	0.160	0.169	3.9
36	Aldrin	1144	1143	0.133	1.171	2.3
37	Heptachlor epoxide	1205	1204	0.144	0.138	3.0
38	*p*,*p*'-DDE	1297	1296	0.500	0.514	2.0
39	Endrin	1326	1325	0.033	0.025	19.5
40	*p*,*p*'-DDD	1358	1356	0.760	0.658	10.2
41	*p*,*p*'-DDT	1409	1407	0.396	0.373	4.2
42	α-Endosulfan	1258	1256	0.071	0.063	8.4
IS	d_{12}-Chrysene	1475	1473	1.000	1.000	-

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a Relative response factors determined for 40 ng on column injection.

b Not analyzed.

c Benzidine not detected by GC/MS at ≦ 40 ng on column.

TABLE 11. RELATIVE RESPONSE TIME AND RELATIVE RESPONSE FACTORS OF 42 BASE/NEUTRAL/PESTICIDE COMPOUNDS ANALYZED USING SE-54 FUSED SILICA CAPILLARY

Compound No.	Compound	Scan No.	Relative retention time (RRT)	Relative response factor (RRF)[a] 10 ng on column	40 ng on column
1	Bis(2-chloroethyl) ether	242	0.544	0.515 ± 0.095	0.533 ± 0.070
2	1,3-Dichlorobenzene	258	0.580	0.478 ± 0.070	0.502 ± 0.069
3	1,2-Dichlorobenzene	288	0.647	0.491 ± 0.063	0.488 ± 0.076
4	Hexachloroethane	327	0.735	0.245 ± 0.041	0.248 ± 0.054
5	N-Nitroso-di-n-propylamine	330	0.742	0.084 ± 0.015	0.078 ± 0.010
6	Nitrobenzene	345	0.775	0.615 ± 0.141	0.609 ± 0.158
7	Bis(2-chloroethoxy)methane	424	0.953	0.720 ± 0.114	0.658 ± 0.078
8	1,2,4-Trichlorobenzene	440	0.989	0.474 ± 0.035	0.419 ± 0.028
9	Naphthalene	447	1.004	2.039 ± 0.113	1.635 ± 0.239
IS	d_8-Naphthalene	445	1.000	1.000	1.000
10	Hexachlorobutadiene	482	0.476	0.305 ± 0.059	0.310 ± 0.093
11	Hexachlorocyclopentadiene	604	0.597	0.057 ± 0.019	0.079 ± 0.035
12	2-Chloronaphthalene	644	0.636	1.020 ± 0.087	1.033 ± 0.182
13	Acenaphthylene	716	0.708	1.848 ± 0.172	1.603 ± 0.237
14	2,6-Dinitrotoluene	732	0.723	0.229 ± 0.019	0.245 ± 0.066
15	Acenaphthene	750	0.741	1.172 ± 0.122	1.057 ± 0.122
16	2,4-Dinitrotoluene	799	0.790	0.211 ± 0.307	0.241 ± 0.064
17	Fluorene	839	0.829	1.274 ± 0.130	1.184 ± 0.105
18	4-Chlorophenyl phenyl ether	850	0.840	0.442 ± 0.056	0.405 ± 0.041
19	Diethylphthalate	852	0.842	1.367 ± 0.290	1.290 ± 0.132
20	4-Bromophenyl phenyl ether	934	0.923	0.271 ± 0.031	0.253 ± 0.027
21	Hexachlorobenzene	950	0.939	0.308 ± 0.023	0.279 ± 0.049
22	Phenanthrene	1007	0.995	1.596 ± 0.230	1.384 ± 0.164
23	Anthracene	1015	1.003	1.632 ± 0.072	1.290 ± 0.098
IS	d_{10}-Anthracene	1012	1.000	1.000	1.000
24	Di-n-butylphthalate	1149	0.775	4.264 ± 1.469	3.873 ± 1.364
25	Fluoranthene	1221	0.823	2.797 ± 0.252	2.892 ± 0.320
26	Pyrene	1259	0.849	2.713 ± 0.268	2.687 ± 0.282
27	Benzidine[b]	ND	-	-	-

(continued)

TABLE 11 (continued)

Compound No.	Compound	Scan No.	Relative retention time (RRT)	Relative response factor (RRF)[a] 10 ng on column	Relative response factor (RRF)[a] 40 ng on column
28	Endosulfan sulfate	1411	0.951	0.094 ± 0.045	0.106 ± 0.041
29	n-Butylbenzylphthalate	1416	0.955	0.892 ± 0.424	1.002 ± 0.564
30	Chrysene	1488	1.003	1.851 ± 0.104	1.640 ± 0.253
31	3,3'-Dichlorobenzidine	1493	1.007	0.148 ± 0.072	0.124 ± 0.074
32	Bis(2-ethylhexyl)phthalate	1534	1.034	1.596 ± 0.811	1.401 ± 0.736
33	Benzo[a]pyrene	1715	1.156	1.000 ± 0.269	0.866 ± 0.180
34	Dibenzo[a,h]anthracene	1880	1.268	0.661 ± 0.291	0.521 ± 0.172
35	γ-BHC[c]	994	0.982	0.157 ± 0.004	0.150 ± 0.023
36	Aldrin	1154	0.778	0.906 ± 0.144	0.897 ± 0.336
37	Heptachlor epoxide	1214	0.819	0.127 ± 0.021	0.135 ± 0.036
38	p,p'-DDE	1306	0.881	0.611 ± 0.060	0.601 ± 0.097
39	Endrin	1339	0.903	0.029 ± 0.021	0.024 ± 0.009
40	p,p'-DDD	1366	0.921	1.017 ± 0.206	0.929 ± 0.173
41	p,p'-DDT	1417	0.955	0.288 ± 0.081	0.327 ± 0.177
42	α-Endosulfan	1267	0.854	0.072 ± 0.015	0.072 ± 0.017
IS	d_{12}-Chrysene	1483	1.000	1.000	1.000

a Number of GC/MS runs is 8.

b Not detected by GC/MS at 10 ng or 40 ng injections.

c Relative to d_{10}-anthracene.

TABLE 12. RELATIVE RESPONSE TIME AND RELATIVE RESPONSE FACTORS OF ACIDS ANALYZED USING SE-54 FUSED SILICA CAPILLARY

Compound No.	Compound	Scan No.	Relative retention time (RRT)	Ion used for quantitation	Relative response factor (RRF) 10 ng on column	Relative response factor (RRF) 40 ng on column[a]
1	Phenol	197	0.618	94	0.503; 0.513	0.654
2	2-Chlorophenol	204	0.639	128	0.358; 0.358	0.434
3	2,4-Dimethylphenol	296	0.928	122	0.213; 0.351	0.389
4	2,4-Dichlorophenol	311	0.975	162	0.223; 0.223	0.371
IS	d_{10}-Naphthalene	319	1.000	136	1.000	1.000
5	2,4,6-Trichlorophenol	412	0.665	196	0.173; 0.173	0.319
6	2,4-Dinitrophenol	491	0.792	184	0.010; 0.019	0.101; 0.095
7	4-Nitrophenol	503	0.811	65	0.121; 0.119	0.318; 0.309
8	4,6-Dinitro-*o*-cresol	542	0.874	198	0.040; 0.041	0.141; 0.131
9	Pentachlorophenol	606	0.977	266	0.082; 0.082	0.140; 0.151
IS	d_{10}-Anthracene	620	1.000	188	1.000	1.000

[a] Relative response factors (RRF) determined from a single GC/MS run for compounds 1-5.

TABLE 13. COMPARISON OF THE ABSOLUTE PEAK COUNTS AND RELATIVE RESPONSE FACTORS BY CONNECTING THE FUSED SILICA CAPILLARY COLUMN TO THE ION SOURCE WITH AND WITHOUT A TRANSFER LINE

Compound No.	Compound	Ion selected for quantitation	Peak height (absolute counts)[a] With transfer line to MS	Peak height (absolute counts)[a] Without transfer line to MS	Relative response factor (RRF)[a] With transfer line to MS	Relative response factor (RRF)[a] Without transfer line to MS
1	Bis(2-chloroethyl) ether	93	14,112	8,528	0.696	0.423
2	1,3-Dichlorobenzene	146	12,992	8,400	0.640	0.417
3	1,2-Dichlorobenzene	146	12,992	9,444	0.640	0.468
4	Hexachloroethane	117	5,368	5,320	0.265	0.264
5	N-Nitroso-di-*n*-propylamine	130	1,730	1,021	0.085	0.051
6	Nitrobenzene	77	18,272	15,536	0.901	0.771
7	Bis(2-chloroethoxy)methane	93	12,832	12,992	0.632	0.644
8	1,2,4-Trichlorobenzene	180	10,784	9,360	0.532	0.464
9	Naphthalene	128	41,408	42,112	2.041	2.089
IS	d_8-Naphthalene	136	81,152	80,640	1.000	1.000
10	Hexachlorobutadiene	225	6,288	6,248	0.389	0.185
11	Hexachlorocyclopentadiene	237	1,426	2,952	0.088	0.087
12	2-Chloronaphthalene	162	21,952	30,240	1.360	0.895
13	Acenaphthylene	152	29,728	50,112	1.841	1.483
14	2,6-Dinitrotoluene	169	4,400	8,336	0.273	0.247
15	Acenaphthene	154	18,112	31,552	1.122	0.934
16	2,4-Dinitrotoluene	169	4,152	8,994	0.257	0.291
17	Fluorene	166	17,120	35,840	1.060	1.061
18	4-Chlorophenyl phenyl ether	204	6,168	11,904	0.382	0.352
19	Diethylphthalate	149	8,304	23,648	0.514	0.700
20	4-Bromophenyl phenyl ether	248	1,194	7,144	0.074	0.211
21	Hexachlorobenzene	284	5,792	11,184	0.359	0.331
22	Phenanthrene	178	16,510	37,630	1.023	1.114
23	Anthracene	178	21,120	59,136	1.308	1.750
IS	d_{10}-Anthracene	188	64,576	135,168	1.000	1.000
24	Di-*n*-butylphthalate	149	3,992	14,976	1.476	1.370
25	Fluoranthene	202	9,360	23,648	3.462	2.164
26	Pyrene	202	6,696	27,936	2.476	2.556
27	Benzidine[b]	184	ND	ND	ND	ND
28	Endosulfan sulfate	272	ND	832	ND	0.076
29	*n*-Butylbenzylphthalate	149	621	2,988	0.230	0.273
30	Chrysene	228	3,508	18.176	1.297	1.663
31	3,3'-Dichlorobenzidine	252	ND	825	ND	0.075
32	Bis(2-ethylhexyl)phthalate	149	921	4,272	0.341	0.391
33	Benzo[*a*]pyrene	252	2,192	4,256	0.811	0.389
34	Dibenzo[*a*,*h*]anthracene	278	2,692	3,796	0.996	0.347
35	γ-BHC[c]	183	-	5,432	-	0.161
36	Aldrin	66	2,644	7,488	0.978	0.685
37	Heptachlor epoxide	353	630	1,046	0.233	0.096
38	*p*,*p*'-DDE	246	1,908	5,440	0.706	0.498
39	Endrin	317	ND	533	ND	0.049
40	*p*,*p*'-DDD	235	1,768	6,712	0.654	0.614
41	*p*,*p*'-DDT	235	846	3,632	0.313	0.607
42	α-Endosulfan	195	ND	832	ND	0.076
IS	d_{12}-Chrysene	240	10,816	43,712	1.000	1.000

[a] Amount injected on column is 10 ng for compounds and 40 ng for internal standards (IS).

[b] Benzidine not detected by GC/MS at < 40 ng on column.

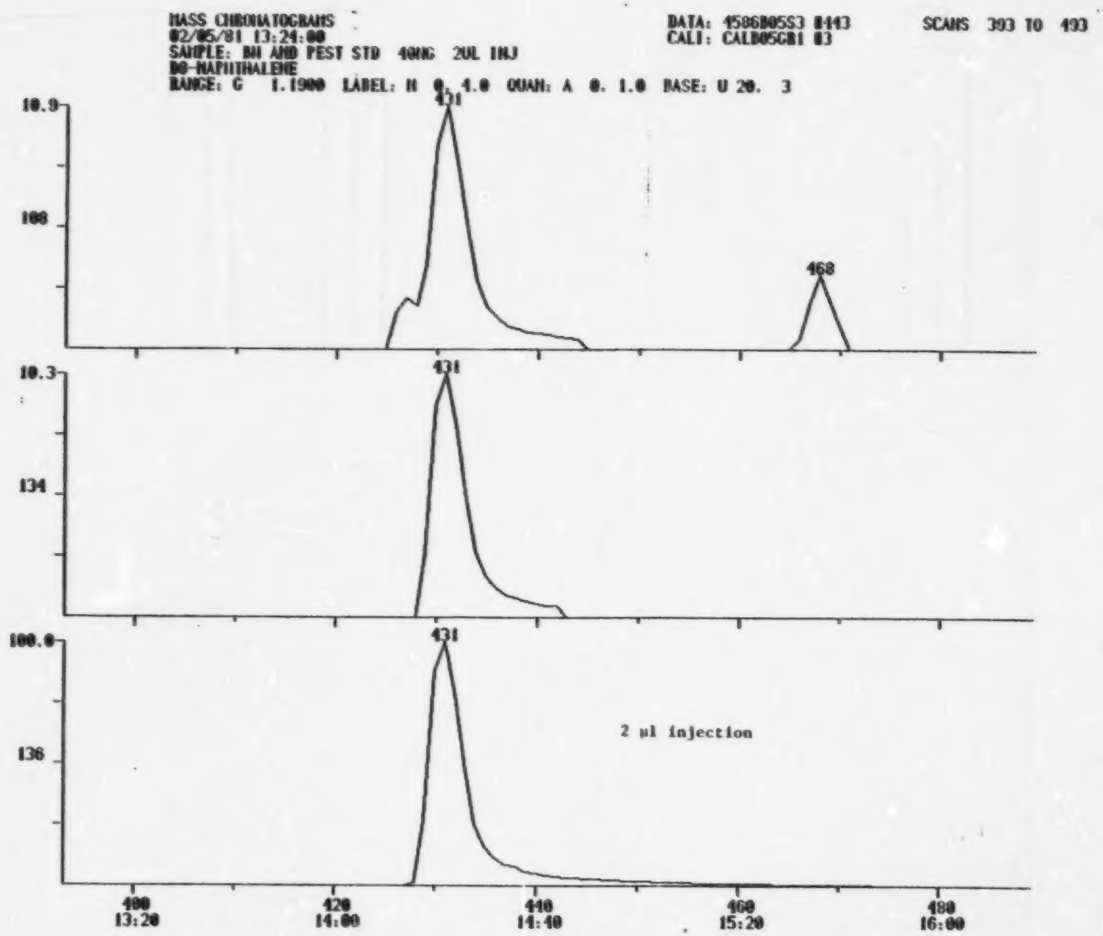

Figure 14. Extracted ion current plots (m/e 136, m/e 134, and m/e 108) for d_8-naphthalene spiked into a base/neutral/pesticide test mixture.

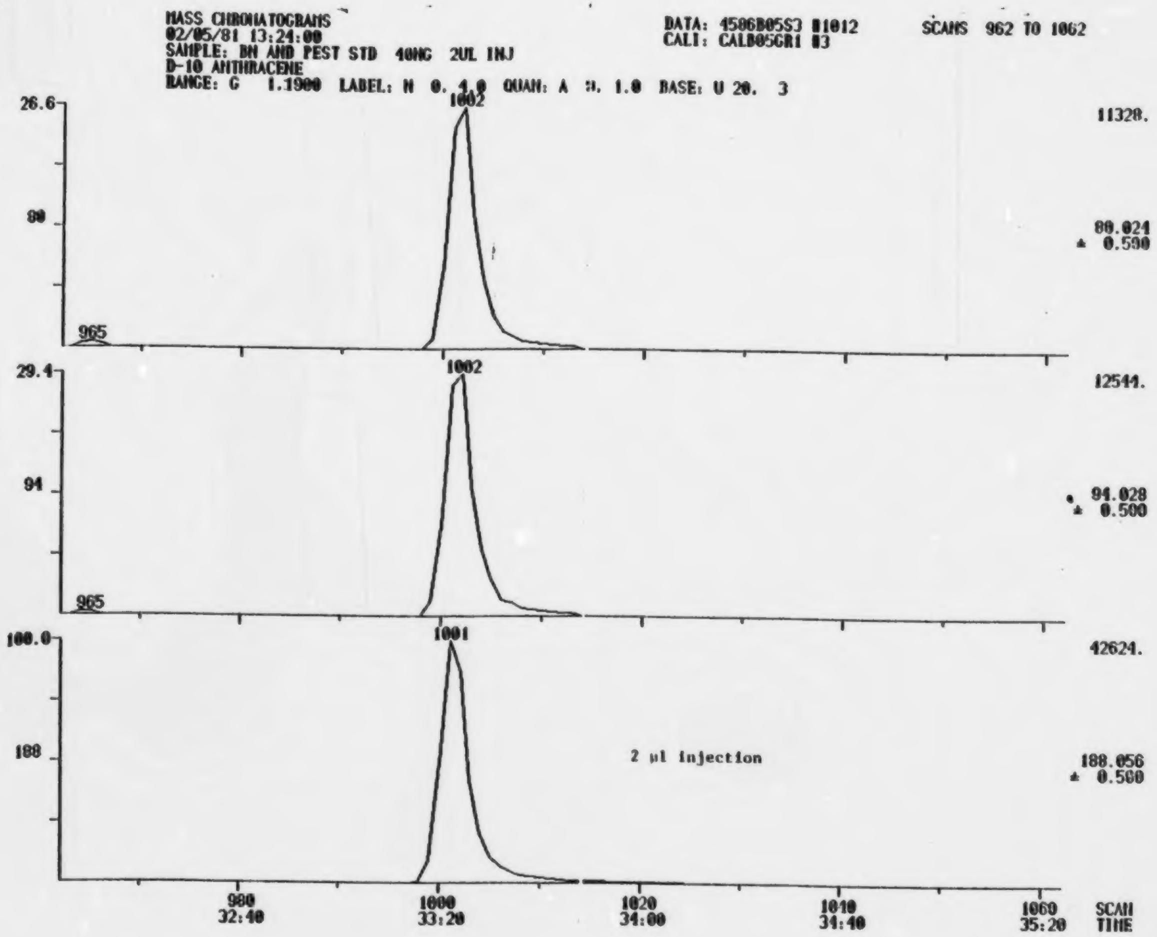

Figure 15. Extracted ion current plots (m/e 188, m/e 94, and m/e 80) for d_{10}-anthracene spiked into a base/neutral/pesticide test mixture.

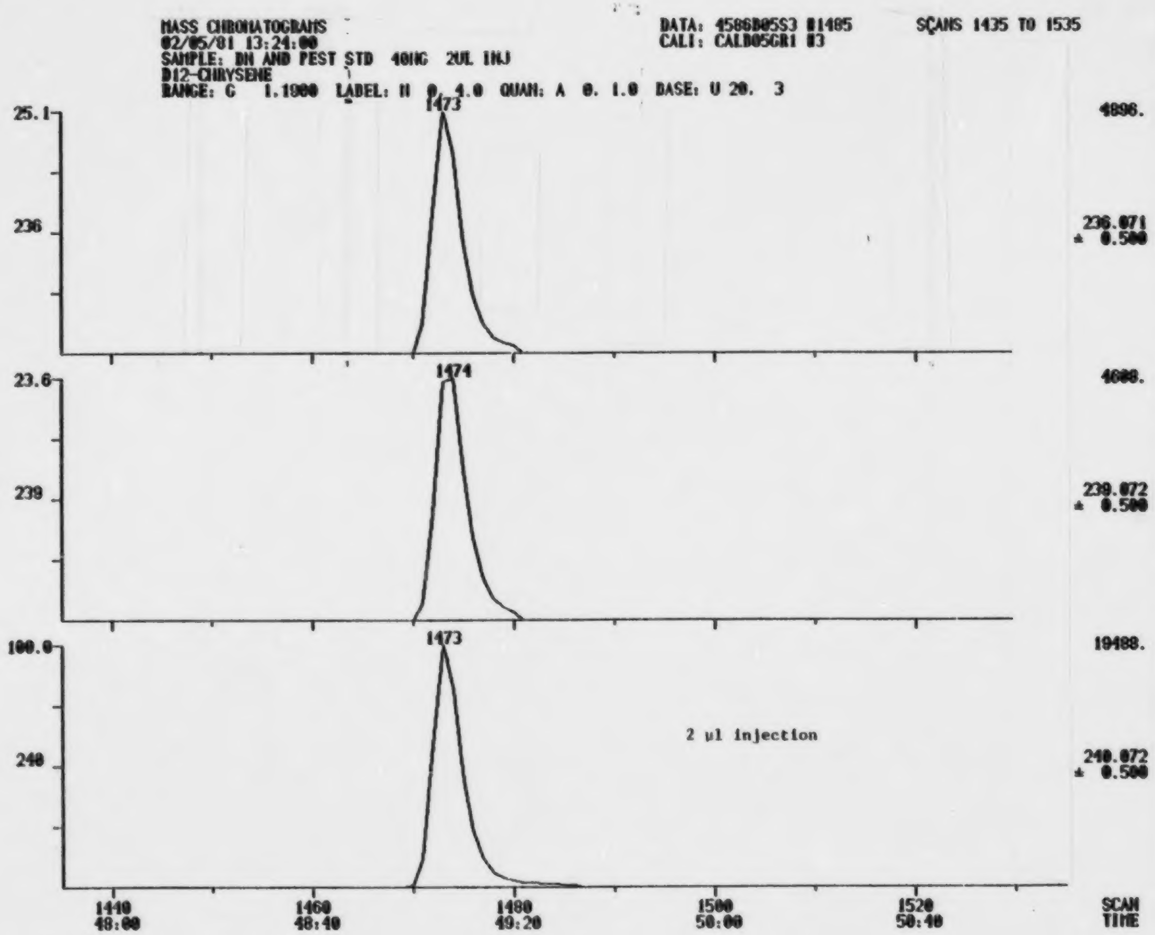

Figure 16. Extracted ion current plots (m/e 240, m/e 239, and m/e 236) for d_{12}-chrysene spiked into a base/neutral/pesticide test mixture.

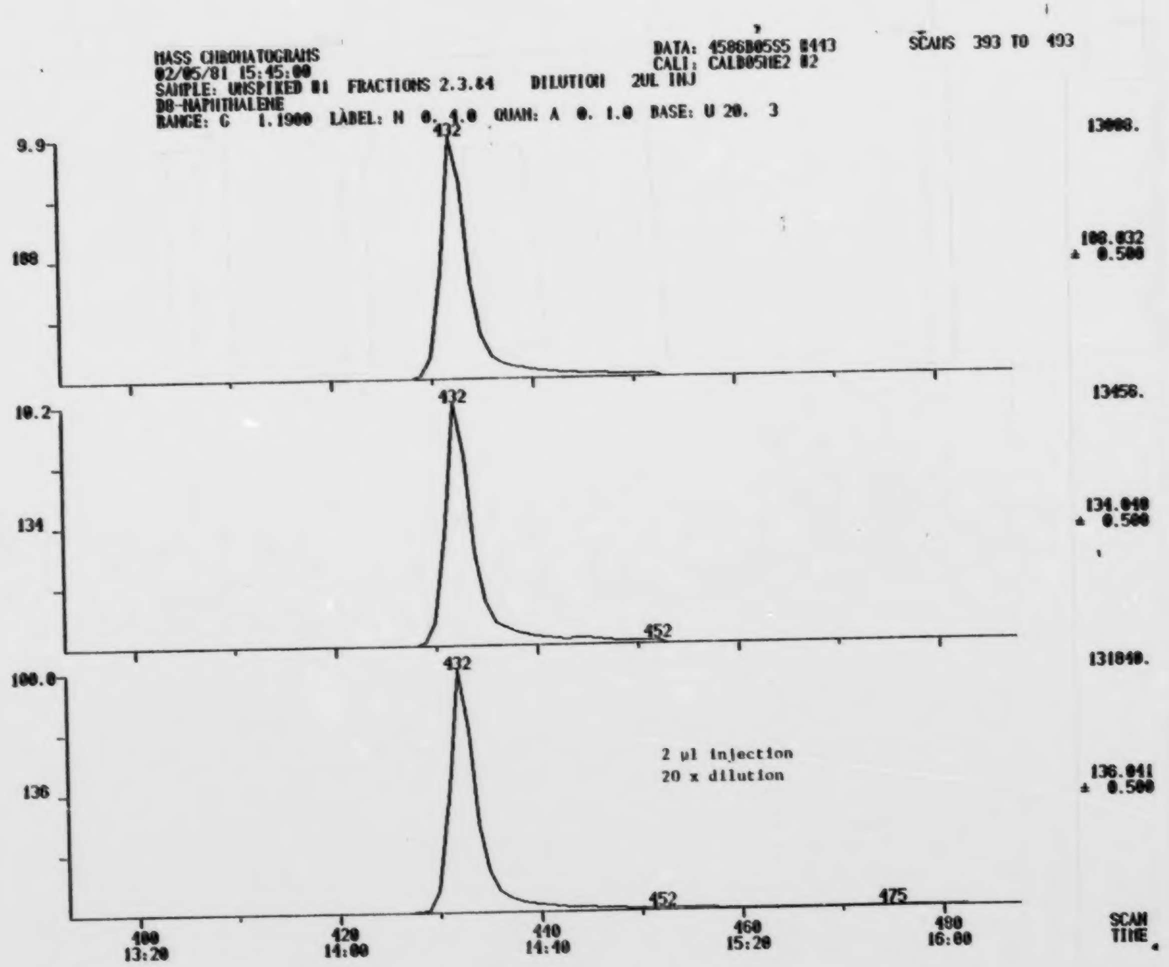

Figure 17. Extracted ion current plots (m/e 136, m/e 134, and m/e 108) for d_8-naphthalene spiked into the combined eluent (fractions II through IV) obtained by silica gel cleanup/fractionation of the NBS sediment extract.

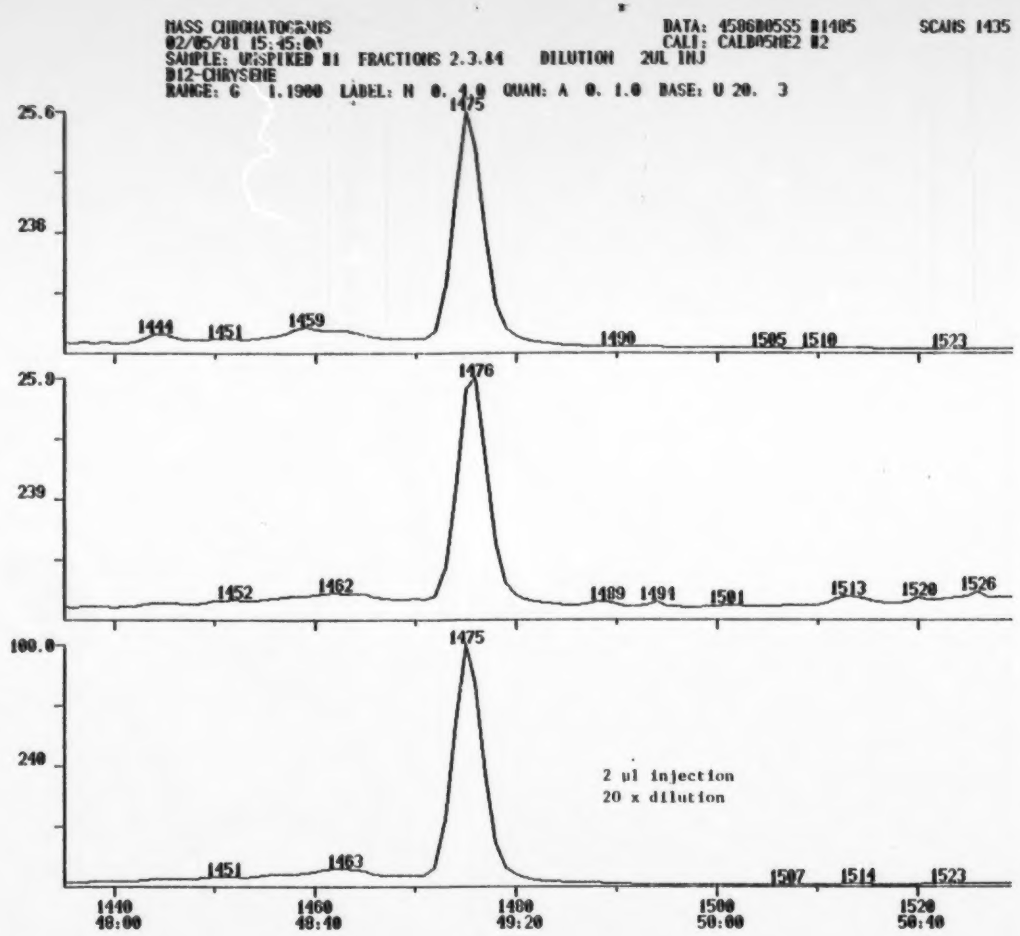

Figure 18. Extracted ion current plots (m/e 240, m/e 239, and m/e 236) for d_{12}-chrysene spiked into the combined eluent (fractions II through IV) obtained by silica gel cleanup/fractionation of the NBS sediment extract.

A series of dilutions (1:10, 1:20, and 1:40) were performed to study this phenomenon. Figures 19 through 21 show the mass chromatograms for the ions at m/e 188, 94, and 80 characteristic for d_{10}-anthracene. It can be noted that the peak height of the precursor peak decreases as the dilution of the sample increases, and only becomes zero when the volume of injection is 0.5 µl at 1:10 dilution (see Figure 22). In all cases where double peaking was observed, the retention time of d_{10}-anthracene in the standard fell between the two peaks.

Double peaking was also reported (John McGovern, Southwest Research Institute, personal communication, 1981) when samples of the same sediment were analyzed for priority pollutants. In that case, the solution to the double peaking phenomenon was found to be a change in the solvent. A change from methanol to dichloromethane showed an increase in peak area, an improvement in peak shape, and the elimination of the precursor peak.

Two possible explanations for the formation of double peaks are given below. Based on the results of the dilution experiments, it appears that the injection technique and the column overload may have caused this phenomenon. Splitless injection produces a solvent peak of about 30 cm in length and a peak height 100 to 300 times the film thickness in the column.[4] The carrier gas causes the solvent peak to migrate at rates that will depend on the thickness of the solvent layer. It has been shown that after a short migration through the column the solvent peak will exhibit a very steep back slope with the front very long and flat. When analytes less volatile than the solvent reach the column, the bands of such substances may be shortened since they move against a thick, increasing solvent peak, and may become split by interfering coelutants in the sample. By decreasing the volume of the solvent injected onto the capillary column, the so-called "solvent effect" phenomenon was reduced and the double peaking phenomenon seemed to disappear (see Figure 22). However, the decrease in the volume of solvent would compromise significantly the reproducibility of the splitless injection.

It is widely recognized by chromatographers that one major drawback of the splitless injection is its poor reproducibility (standard deviations of ± 10 to 20%). Furthermore, the reproducibility becomes even poorer (standard deviations of ± 30 to 40%) when the volume of solvent is reduced below 0.7 to 0.8 µl. Significantly improved reproducibilities for the injection technique (± 5% standard deviation) have recently been reported with an on-column injector.[5] Therefore, the on-column injection with injection volumes of 0.2 to 0.5 µl should be investigated in future studies. The effect of the type of solvent should also be investigated. Methanol did not appear to cause the double peaking effect since the standards analyzed contained up to 50% methanol by volume and all the sediment extracts were in dichloromethane.

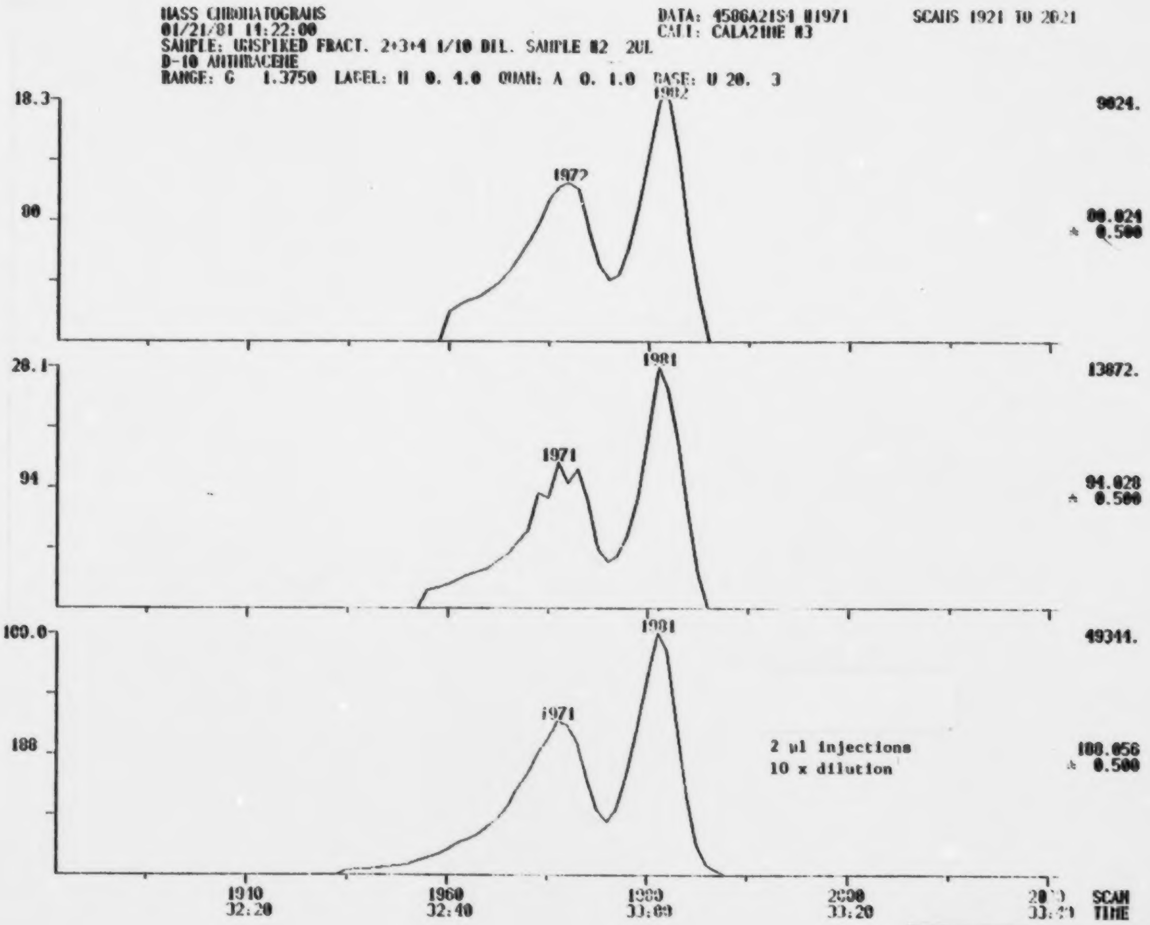

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Figure 19. Extracted ion current plots (m/e 188, m/e 94, and m/e 80) for d_{10}-anthracene spiked into the combined eluent (fractions II through IV) obtained by silica gel cleanup/fractionation of the NBS sediment (10X dilution).

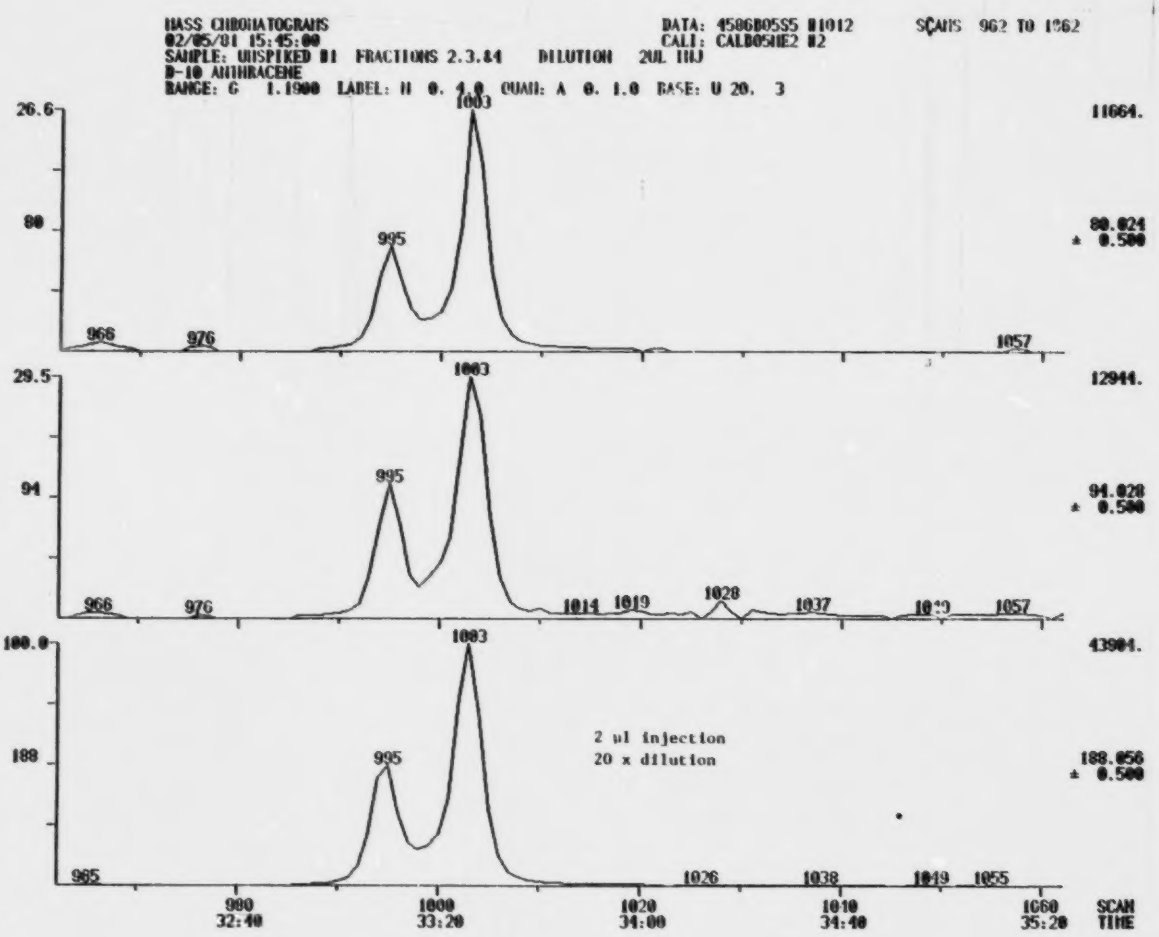


Figure 20. Extracted ion current plots (m/e 188, m/e 94, and m/e 80) for d_{10}-anthracene spiked into the combined eluent (fractions II through IV) obtained by silica gel cleanup/fractionation of the NBS sediment (20X dilution).

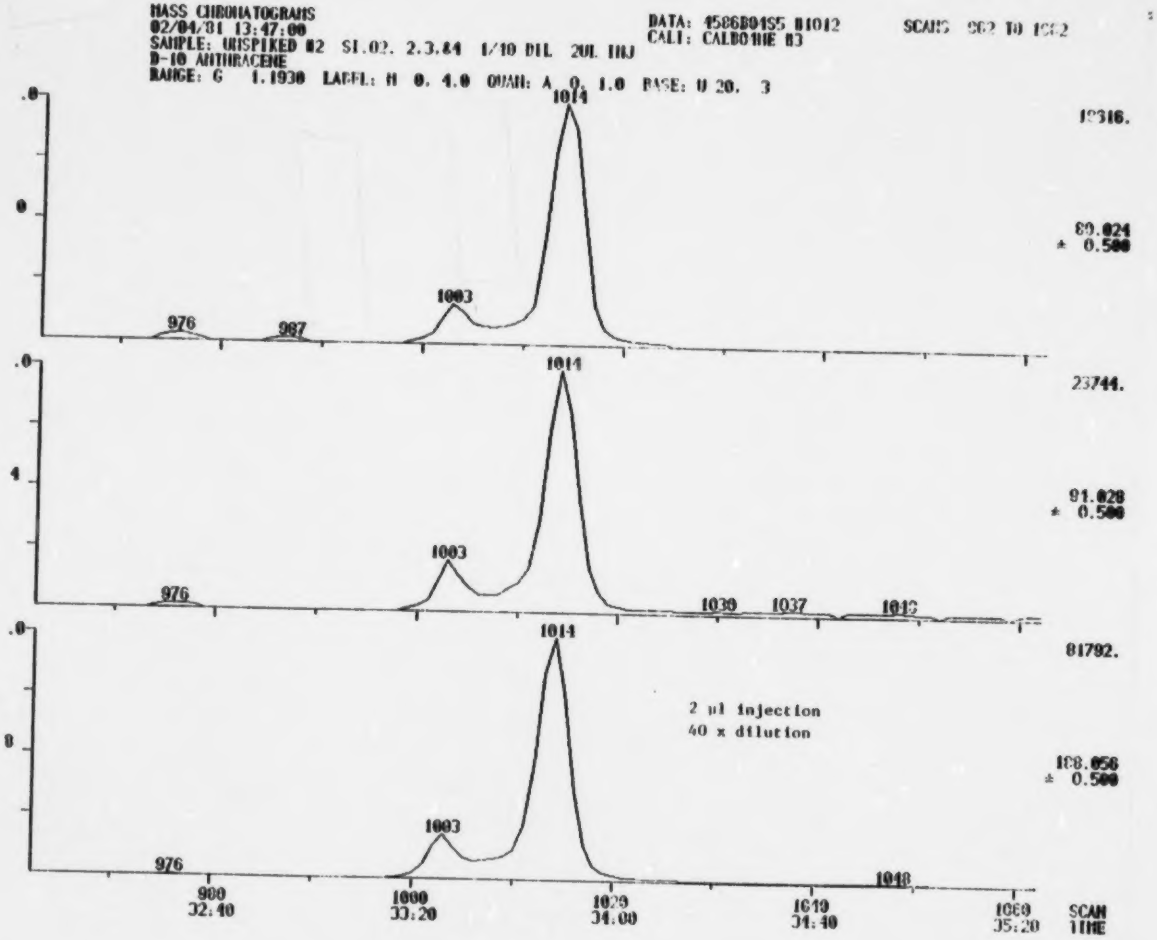


Figure 21. Extracted ion current plots (m/e 188, m/e 94, and m/e 80) for d_{10}-anthracene spiked into the combined eluent (fractions II through IV) obtained by silica gel cleanup/fractionation of the NBS sediment (40X dilution).

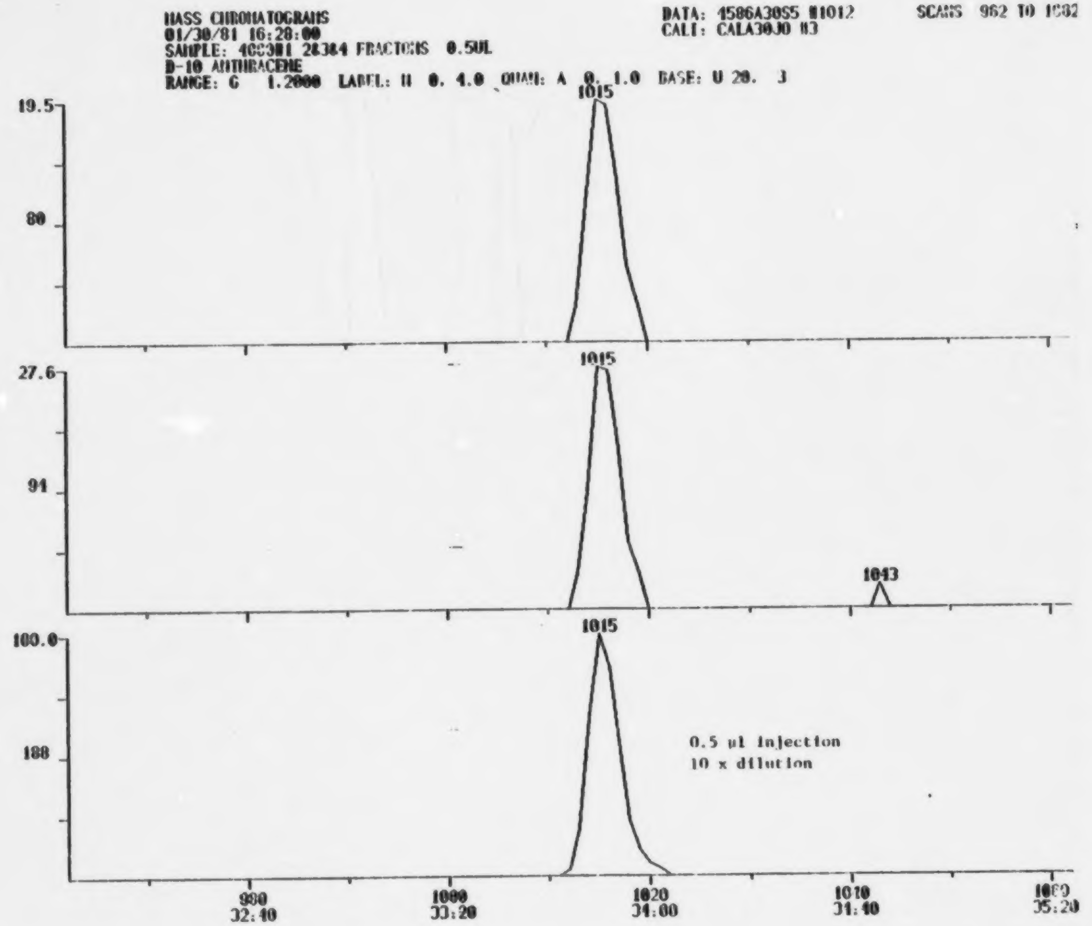


Figure 22. Extracted ion current plots (m/e 188, m/e 94, and m/e 80) for d_{10}-anthracene spiked into the combined eluent (fractions II through IV) obtained by silica gel cleanup/fractionation of the NBS sediment (10X dilution); 0.5 µl injection.

Another possible explanation of the double peaking phenomenon may be related to the column performance. When using capillary columns, especially the narrow bore type, column overloading may be expected. The overload phenomenon may be the result of the saturation of the liquid phase, due to the massive amount of components eluting in the midregion of the chromatogram. This is substantiated by the observation of leading peaks for the precursor when double peaking occurred. Generally, leading peaks result from insufficient vaporization of the sample or from column overload.[6] The insufficient vaporization effect is excluded here since the temperature of the injection port was quite high (275°C) and no difference was observed between injections at 225°C and injections at 275°C. The column overload effect that might have caused leading peaks and double peaking is very likely to have occurred in the liquid phase for the following reasons:

1. Leading peaks.

2. Change in retention time.

3. The precursor peak decreases as the sample dilution increases.

When the liquid phase is overloaded (saturated with solute), additional solute will go into the gas phase and it will start traveling through the column. When the solute comes into contact with fresh liquid phase, it will dissolve until an equilibrium is reached. As soon as the proper conditions for compound to elute are reached, overloaded regions will travel faster than non-overloaded regions, causing both leading peaks and perhaps double peaking phenomena.

To overcome overloading the capillary column, the injection of samples as dilute solutions is recommended. Use of wider bore columns with increased thickness of the liquid phase film (0.5 to 1 µl), which would allow for increased sample capacity, is also recommended.

SECTION 6

TENTATIVE IDENTIFICATION OF COMPONENTS IN THE NBS SEDIMENT EXTRACT

The GC/MS analyses of the four silica gel fractions generated from the NBS sediment extract resulted in the tentative identification of 106 base/neutral compounds, without considering the various isomers of many of these compounds. Table 14 is a comprehensive list of these compounds, grouped by compound class, and Tables 15 through 17 contain the compounds identified in each fraction, in their order of elution from the SE-54 fused silica capillary column. Eleven acidic compounds were identified in the acidic sediment extract. Table 18 contains the identities of these compounds in their order of elution from the SE-54 fused silica capillary column. All identifications are tentative with the exception of the priority pollutants given in Table 1 for which GC retention times were obtained, regardless of the fact that most of the mass spectra generated, when compared against mass spectra in the EPA/NIH mass spectral data base,[1] provided large FIT indices. When FIT equals 1,000, it is a perfect match. Furthermore, identifications for specific positional isomers, such as dimethylnaphthalenes and trimethylnaphthalenes, could not be provided because time and funds did not permit the required analyses with authentic standards. Consequently, concentrations of these compounds have not been determined. However, extracted ion currents for the two or three most intense peaks in the mass spectra of many compounds have been submitted to the USEPA project officer, should it be necessary to estimate these concentrations later.

In brief, the procedures used to tentatively identify each GC peak involved selection of an enhanced peak mass spectrum as the result of a background subtraction routine and the comparison of this mass spectrum against mass spectra in the EPA/NIH library, which contains almost 25,000 mass spectra. The EPA/NIH library search provided FIT, PURITY, and RFIT indices which were used as a first guess in compound identity. Many of the mass spectra were also manually interpreted, especially when a match via library search was unsuccessful.

A limiting factor in most mass spectra identifications is the purity of a compound (coeluting peaks would give mass spectra with large FIT indices but low PURITY indices) and the availability of the compound mass spectrum in the data base. Whenever a tentative identification was made, either by library search routines or by manual interpretation, mass chromatograms for the most intense ions in the mass spectrum were obtained. This allowed in many instances identification of other isomers and assignment of coeluting peaks. Although the library search did indicate in many cases the positional isomers that best matched a particular unknown mass spectrum, this was not considered reliable enough in confirming the compound identity.

TABLE 14. TENTATIVELY IDENTIFIED COMPOUNDS IN THE NBS SEDIMENT EXTRACT

Compound	Identified in fraction			
	I	II	III	IV
Aliphatic hydrocarbons				
Alkane (low M.W.)				X
Heptane		X		
$C_{12}H_{16}$ (isomers)		X		
$C_{13}H_{18}$ (isomers)		X		
Aromatic hydrocarbons				
Benzene		X		
Toluene		X		
Xylene (isomers)		X		
C_8-Alkylbenzene		X		
Styrene				X
Polycyclic aromatic hydrocarbons				
Naphthalene*		X	X	
1-Methylnaphthalene		X	X	
2-Methylnaphthalene		X	X	
Ethylnaphthalene		X	X	
Dimethylnaphthalene (isomers)		X	X	
C_3-Alkylnaphthalene (isomers)		X	X	
C_4-Alkylnaphthalene (isomers)		X		
C_5-Alkylnaphthalene (isomers)		X		
1-Phenylnaphthalene			X	
2-Phenylnaphthalene			X	
Phenylmethylnaphthalene (isomers)			X	
Acenaphthylene*	X	X	X	X
Biphenyl			X	
Terphenyl			X	
Acenaphthene*		X	X	X
Diphenyl ether		X		
Fluorene*			X	X
Methylfluorene (isomers)			X	
Dimethylfluorene (isomers)			X	
C_3-Alkylbiphenyl			X	
Phenanthrene*		X	X	X
Anthracene*		X	X	X
Methylphenanthrene (isomers)			X	
Methylanthracene (isomers)			X	
Ethylphenanthrene or ethylanthracene			X	
Dimethylphenanthrene (isomers)			X	
Dimethylanthracene (isomers)			X	
C_3-Alkylphenanthrene (isomers)			X	
C_3-Alkylanthracene (isomers)			X	

(continued)

TABLE 14 (continued)

Compound	Identified in fraction I	II	III	IV
4H-Cyclopenta[def]phenanthrene			X	
Fluoranthene*			X	X
Pyrene*		X	X	X
Methylfluoranthene (isomers)			X	
Methylpyrene (isomers)			X	
Benzphenanthrene (isomers)			X	
Benzanthracene (isomers)			X	
Chrysene*			X	X
Methylbenzanthracene (isomers)			X	
Methylchrysene (isomers)			X	
Dimethylbenzanthracene (isomers)			X	
Dimethylchrysene (isomers)			X	
Dimethyltriphenylene (isomers)			X	
1,1'-Binaphthyl			X	
1,2'-Binaphthyl			X	
2,2'-Binaphthyl			X	
Benzofluoranthene (isomers)			X	
Benzo[a]pyrene*			X	X
Perylene			X	
Methylbenzofluoranthene (isomers)			X	
Methylbenzopyrene (isomers)			X	
Dibenzoanthracene (isomers)			X	
Benzochrysene (isomers)			X	
Dibenzo[a,h]anthracene*			X	X
Benzo[g,h,i]perylene			X	
Indeno[1,2,3-cd]pyrene			X	
Sulfur-containing heterocyclics				
Di-n-propylthiophene (isomers)			X	
Dibenzothiophene		X	X	
Methyldibenzothiophene (isomers)		X	X	X
Dimethyldibenzothiophene (isomers)		X	X	
Dimethylnaphthothiophene (isomers)		X	X	
Ethylnaphthothiophene		X		
C_3-Alkyldibenzothiophene		X		
C_4-Alkyldibenzothiophene		X		
Benzonaphthothiophene (isomers)			X	
Methylbenzonaphthothiophene (isomers)			X	
Benzophenanthrenothiophene[a]			X	
Anthrabenzothiophene[b]			X	
$C_{18}H_{10}S$ (isomers)[c]			X	
Dinaphthothiophene (isomers)[d]			X	
Thioxanthene			X	
Oxygen-containing heterocyclics				
Methyldibenzofuran (isomers)			X	

(continued)

TABLE 14 (continued)

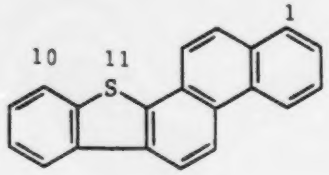
Compound	Identified in fraction			
	I	II	III	IV
Aldehydes and ketones				
Benzaldehyde				X
1-Phenylethanone				X
Fluorenone				X
Methylfluorenone (isomers)				X
Methylanthrone (isomers)				X
Cyclopenta[*d*,*e*,*f*]phenanthrenone				X
Benzofluorenone (isomers)				X
Methylbenzofluorenone (isomers)				X
Benzanthracenequinone (isomers)				X
Indenoanthracenone (isomers)[e]				X
$C_{19}H_{10}O$ (isomers)[f]				X
Pesticides				
p,*p*'-DDE*			X	
p,*p*'-DDD*				X
p,*p*'-DDT*		X	X	
γ-BHC*		X		
Phenols				
Phenol*[g]				
Miscellaneous compounds				
Benzoic acid[g]				
Ethylhexanol				X
1-(2-Propenyloxy)-heptane				X
Acetic acid phenyl ethyl ester				X
1-H Indene				X
Di-*n*-butylphthalate*	X		X	X
n-Butylbenzylphthalate*				X
Bis(2-ethylhexyl)phthalate*			X	X
Endosulfan sulfate*				X
Methyl cholestane				X
$C_{28}H_{46}O$ (possible ergosta-5,8-diene-3-ol)		X		
Sulfur	X			
Fatty acids[g,h]				

* Confirmed with authentic compounds.

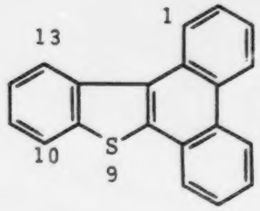
(continued)

TABLE 14 (continued)

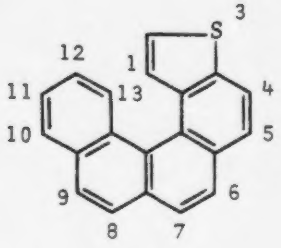
a Possible structures:



Benzo[b]phenanthro[2,1-d]thiophene

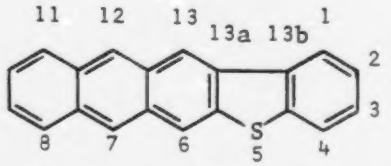


Benzo[b]phenanthro[9,10-d]thiophene

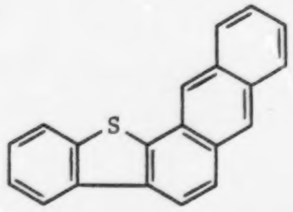

3
S
12
1
11
13
4
10
5
9
6
8
7

Benzo[5,6]phenanthro[3,4-b]thiophene

b Possible structures:

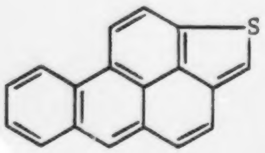

11
12
13
13a
13b
1
2
3
8
7
6
S
5
4

Anthra[2,3-b]benzo[d]thiophene



Anthra[1,2-b]benzo[d]thiophene

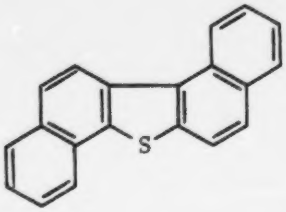
c Possible structure:



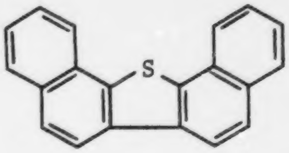
Sulfur-containing PAH similar to 1H-Indeno[6,7,1-mna]anthracene

TABLE 14 (continued)

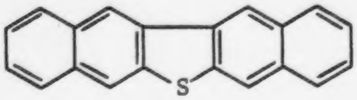
d Possible structures:



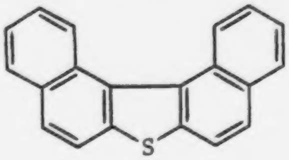
Dinaphtho[1,2-b:1',2'-d]thiophene



Dinaphtho[2,1-b:2',1'-d]thiophene

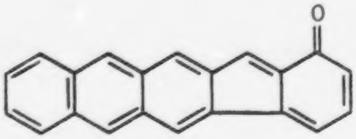


Dinaphtho[2,3-b:2',3'-d]thiophene

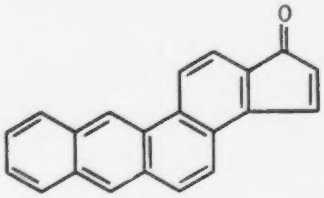


Dinaphtho[2,1-b:1',2'-d]thiophene

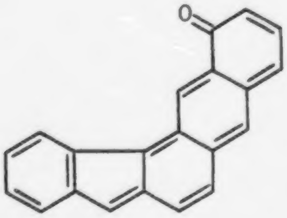
e Possible structures:



1H-Indeno[1,2-b]anthracene-1-one



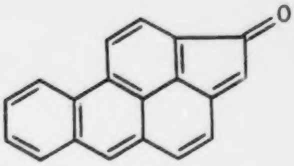
1H-Indeno[5,4-a]anthracene-1-one



1H-Indeno[1,2-a]anthracene-1-one

TABLE 14 (continued)

f Possible structure:



1H-Indeno[6,7,1-mna]anthracene-1-one

g Identified in the acidic extract.

h Nine fatty acids were tentatively identified in the acidic extract by searching for fragment ions at m/e 60 and m/e 73.

TABLE 15. IDENTIFICATION OF COMPONENTS IN FRACTION II OF THE NBS SEDIMENT EXTRACT

GC peak No.	Tentatively identified component	Scan No.[a]	Characteristic ions in mass spectrum
1	Unknown	137	56 (100), 69 (68), 84 (40)
2	Benzene	145	56 (100), 78 (82), 69 (67)
3	Heptane	155	57 (100), 71 (90), 56 (59)
4	Toluene	197	92 (100), 65 (44), 89 (30)
5	Xylene	297	91 (100), 106 (49), 105 (22)
6	Xylene	330	91 (100), 106 (38), 105 (20)
7	d_8-Naphthalene (IS)	874	136 (100), 108 (17), 68 (25)
8	Naphthalene	878	128 (100), 127 (15), 51 (14)
9	2-Methylnaphthalene	1103	142 (100), 141 (94), 115 (38)
10	$C_{12}H_{16}$	1120	145 (100), 160 (14)
11	1-Methylnaphthalene	1136	142 (100), 141 (96), 115 (40)
12	$C_{12}H_{16}$	1155	145 (100), 133 (75), 105 (50)
13	$C_{12}H_{16}$	1203	145 (100), 159 (72), 118 (52)
14	$C_{13}H_{18}$	1275	159 (100), 131 (81), 174 (57)
15	$C_{12}H_{16}$	1295	145 (100), 119 (54), 160 (36)
16	Ethylnaphthalene	1304	141 (100), 156 (41), 115 (21)
17	Dimethylnaphthalene	1317	156 (100), 141 (68), 155 (40)
18	Dimethylnaphthalene	1346	156 (100), 141 (96), 155 (43)
19	Dimethlnaphthalene	1383	141 (100), 156 (85), 155 (27)
20	Dimethylnaphthalene	1389	156 (100), 141 (85), 129 (40)
	Acenaphthylene	1401	152 (100), 151 (19), 150 (14)
21	Dimethylnaphthalene	1411	141 (100), 156 (177), 155 (29)
22	C_8-Alkylbenzene	1424	133 (100), 134 (62), 190 (29)
23	Acenaphthene and diphenyl ether	1467	153 (100), 154 (91), 152 (64), 141 (100)
24	C_3-Alkylnaphthalene	1488	155 (100), 170 (52), 115 (23)
25	C_3-Alkylnaphthalene	1496	155 (100), 170 (47), 115 (18)
26	C_3-Alkylnaphthalene	1524	155 (100), 170 (64), 156 (20)
27	C_3-Alkylnaphthalene	1550	155 (100), 170 (75), 115 (18)
28	C_3-Alkylnaphthalene	1579	170 (100), 159 (88), 153 (23)
29	C_4-Alkylnaphthalene	1605	169 (100), 155 (68), 170 (62)
30	C_4-Alkylnaphthalene	1612	169 (100), 155 (76), 170 (73)
31	C_3-Alkylnaphthalene	1651	170 (100), 155 (92), 169 (24)

(continued)

TABLE 15 (continued)

GC peak No.	Tentatively identified component	Scan No.[a]	Characteristic ions in mass spectrum
32	C_4-Alkylnaphthalene	1669	169 (100), 155 (70), 170 (61)
33	Unknown	1676	167 (100), 169 (99), 168 (98)
34	C_4-Alkylnaphthalene	1701	155 (100), 169 (96), 184 (83)
35	C_4-Alkylnaphthalene	1710	169 (100), 184 (50), 152 (22)
36	C_4-Alkylnaphthalene	1716	169 (100), 184 (66), 153 (18)
37	C_4-Alkylnaphthalene	1722	169 (100), 184 (62), 153 (18)
38	C_4-Alkylnaphthalene	1741	169 (100), 184 (49), 167 (22)
39	C_4-Alkylnaphthalene	1757	169 (100), 184 (78), 155 (34)
40	C_4-Alkylnaphthalene	1793	169 (100), 184 (63), 154 (16)
41	C_4-Alkylnaphthalene	1820	184 (100), 169 (92), 166 (22)
42	C_4-Alkylnaphthalene	1826	169 (100), 141 (60), 184 (22)
43	C_5-Alkylnaphthalene	1853	169 (100), 155 (93), 198 (58)
44	Unknown	1858	196 (100), 195 (72), 97 (29)
45	C_5-Alkylnaphthalene	1899	183 (100), 198 (67), 127 (36)
46	Unknown (S)	1907	196 (100), 195 (42), 198 (25)
47	Dibenzothiophene	1927	184 (100), 139 (20), 92 (19)
48	Unknown (S, M.W. 210)	1929	143 (100), 91 (80), 104 (62)
	γ-BHC	1944	183 (100), 181 (99), 109 (97)
49	d_{10}-Anthracene (IS)	1981	188 (100), 94 (30), 80 (28)
50	Unknown (S)	2038	210 (100), 195 (54), 209 (42)
51	Methyldibenzothiophene	2086	198 (100), 197 (65), 199 (17)
52	Methyldibenzothiophene	2115	198 (100), 197 (63), 199 (18)
53	Ethylnaphthothiophene	2225	197 (100), 212 (54), 198 (15)
54	Dimethylnaphthothiophene	2238	212 (100), 211 (48), 105 (27)
55	Dimethylnaphthothiophene	2259	212 (100), 197 (65), 211 (31)
56	Dimethylnaphthothiophene	2266	212 (100), 211 (60), 105 (35)
57	Dimethylnaphthothiophene	2296	212 (100), 211 (55), 105 (24)
58	Thioxanthene	2354	197 (100), 64 (78)
59	C_3-Alkyldibenzothiophene	2366	211 (100), 226 (72), 212 (20)
60	C_3-Alkyldibenzothiophene	2381	211 (100), 226 (72), 175 (42)
61	C_3-Alkyldibenzothiophene	2390	211 (100), 226 (51), 104 (28)
62	C_3-Alkyldibenzothiophene	2402	226 (100), 211 (50), 225 (23)

(continued)

TABLE 15 (continued)

GC peak No.	Tentatively identified component	Scan No.[a]	Characteristic ions in mass spectrum
63	C_3-Alkyldibenzothiophene	2421	211 (100), 191 (72), 162 (55)
64	Unknown	2440	208 (100), 104 (25), 163 (18)
65	Pyrene	2464	202 (100), 101 (37), 201 (26)
66	C_4-Alkyldibenzothiophene	2485	211 (100), 240 (70), 225 (30)
67	Unknown (S)	2570	222 (100), 221 (78), 111 (39)
68	Unknown (S)	2608	222 (100), 221 (65), 111 (53)
	p,p'-DDT	2756	235 (100), 165 (71), 237 (62)
69	Unknown	2852	159 (100), 171 (28), 160 (17)
70	d_{12}-Chrysene	2904	240 (100), 120 (34), 239 (32)
71	$C_{28}H_{46}O$[b]	3386	365 (100), 159 (49), 366 (33)

[a] Scan speed: 1 second/scan.

[b] Possible ergosta-5,8-diene-3-ol.

TABLE 16. IDENTIFICATION OF COMPONENTS IN FRACTION III OF THE NBS SEDIMENT EXTRACT

GC peak No.	Tentatively identified component	Scan No.[a]	Characteristic ions in mass spectrum
1	d_8-Naphthalene (IS)	867	136 (100), 68 (19), 54 (20)
2	Naphthalene	872	128 (100), 127 (10), 129 (11)
3	2-Methylnaphthalene	1100	142 (100), 141 (92), 115 (40)
4	1-Methylnaphthalene	1134	142 (100), 141 (98)
5	Biphenyl	1269	154 (100), 153 (40), 152 (29)
6	Ethylnaphthalene	1304	141 (100), 156 (52), 115 (27)
7	Dimethylnaphthalene	1315	156 (100), 141 (77)
8	Dimethylnaphthalene	1345	156 (100), 141 (86)
9	Dimethylnaphthalene	1382	141 (100), 156 (80), 115 (25)
10	Dimethylnaphthalene	1388	156 (100), 141 (47), 77 (47)
11	Acenaphthylene	1401	152 (100), 153 (16), 151 (17)
12	Dimethylnaphthalene	1412	141 (100), 156 (75), 115 (25)
13	Acenaphthene	1466	154 (100), 153 (95), 152 (53)
14	Di-n-propylthiophene	1523	168 (100), 139 (38), 169 (12)
15	C_3-Alkylnaphthalene and Di-n-propylthiophene	1524	
16	C_3-Alkylnaphthalene	1550	155 (100), 170 (72), 156 (22)
17	C_3-Alkylnaphthalene	1580	170 (100), 155 (94), 115 (18)
18	C_3-Alkylnaphthalene	1608	170 (100), 155 (94), 156 (26)
19	Fluorene	1642	166 (100), 165 (80), 167 (14)
20	C_3-Alkylnaphthalene	1652	170 (100), 155 (97), 156 (20)
21	C_3-Alkylbiphenyl	1667	181 (100), 196 (33), 165 (34)
22	C_3-Alkylnaphthalene	1683	155 (100), 170 (70), 156 (22)
23	Methyl dibenzofuran	1699	182 (100), 181 (97)
24	Methyl dibenzofuran	1710	182 (100), 181 (95), 152 (25)
25	Methyl dibenzofuran	1721	182 (100), 181 (70), 152 (26)
26	Methyl dibenzofuran	1732	181 (100), 182 (92), 152 (20)
27	Methyl dibenzofuran	1751	182 (100), 181 (99), 152 (22)
28	Methylfluorene and unknown (MW 210)	1802	
29	Unknown (M.W. 210)	1813	195 (100), 210 (37), 180 (28)
30	2-Methylfluorene	1839	165 (100), 180 (80), 89 (25)
31	1-Methylfluorene	1853	165 (100), 180 (83), 89 (25)

(continued)

TABLE 16 (continued)

GC peak No.	Tentatively identified component	Scan No.[a]	Characteristic ions in mass spectrum
32	Unknown (S)	1899	181 (100), 196 (98), 195 (38)
33	Unknown (S)	1908	196 (100), 195 (75), 97 (40)
34	Dibenzothiophene	1929	184 (100), 139 (17), 92 (14)
35	Phenanthrene	1973	178 (100), 179 (16), 176 (15)
36	d_{10}-Anthracene (IS)	1983	188 (100), 94 (19), 80 (18)
37	Anthracene	1989	178 (100), 89 (20), 176 (20)
38	Dimethylfluorene	2028	179 (100), 194 (72), 178 (38)
39	Dimethylfluorene	2038	179 (100), 194 (79), 195 (42)
40	Dimethylfluorene	2051	179 (100), 194 (80), 178 (38)
41	Methyldibenzothiophene	2076	198 (100), 197 (65), 165 (15)
42	Methyldibenzothiophene	2090	198 (100), 197 (84), 165 (16)
43	1-Phenylnaphthalene	2097	204 (100), 203 (95), 202 (74)
44	Methyldibenzothiophene	2107	198 (100), 197 (70), 99 (19)
45	Methyldibenzothiophene	2119	198 (100), 197 (68), 99 (20)
46	3-Methylphenanthrene	2137	192 (100), 191 (53), 189 (28)
47	2-Methylphenanthrene	2151	192 (100), 191 (53), 95 (27)
48	3-Methylanthracene	2160	192 (100), 191 (51), 96 (28)
49	2-Methylanthracene	2174	192 (100), 191 (46), 189 (30)
50	4H-Cyclopenta[def]phenanthrene	2184	190 (100), 189 (84), 95 (73)
51	4-Methylphenanthrene	2197	192 (100), 191 (56), 95 (27)
52	Dimethyldibenzothiophene	2226	212 (100), 211 (36), 213 (17)
53	Dimethyldibenzothiophene	2242	212 (100), 211 (48), 105 (26)
	Di-n-butylphthalate	2250	149 (100), 150 (8)
54	Dimethyldibenzothiophene	2263	very weak
55	2-Phenylnaphthalene	2268	204 (100), 202 (39), 203 (30)
56	Dimethyldibenzothiophene	2274	very weak
57	Ethylphenanthrene or ethylanthracene	2291	191 (100), 206 (60), 189 (30)
58	Dimethylanthracene	2306	206 (100), 95 (50), 189 (32)
59	Dimethylphenanthrene	2318	206 (100), 191 (43), 189 (32)
60	Dimethylnaphthothiophene	2330	212 (100), 197 (70), 95 (43)
61	Dimethylphenanthrene or	2338	206 (100), 191 (32), 189 (27)
62	Dimethylanthracene	2358	206 (100), 191 (50), 89 (23)
63	Dimethylphenanthrene or	2364	206 (100), 205 (56), 204 (50)
64	Dimethylanthracene	2386	206 (100), 191 (58), 189 (30)

(continued)

TABLE 16 (continued)

GC peak No.	Tentatively identified component	Scan No.[a]	Characteristic ions in mass spectrum
65	Fluoranthene	2400	202 (100), 101 (71), 100 (40)
66	Phenyl methylnaphthalene	2425	218 (100), 202 (29), 109 (21)
67	Unknown	2446	208 (100), 104 (29), 163 (22)
68	C_3-Alkylphenanthrene or Alkylanthracene	2466	205 (100), 220 (78), 189 (36)
69	Pyrene	2477	202 (100), 101 (26), 100 (17)
70	Phenyl methylnaphthalene	2502	218 (100), 189 (24), 95 (22)
71	C_3-Alkylphenanthrene or	2511	220 (100), 205 (55), 189 (20)
72	C_3-Alkylanthracene	2523	220 (100), 205 (40), 189 (33)
73	C_3-Alkylphenanthrene or	2537	220 (100), 205 (47), 189 (22)
74	C_3-Alkylanthracene and p,p'-DDE	2547	220 (100), 205 (50), 95 (28)
75	Methylfluoranthene or	2565	216 (100), 215 (93), 108 (72)
76	Methylpyrene	2599	216 (100), 215 (90), 108 (40)
77	Methylfluoranthene or	2638	216 (100), 215 (99), 95 (90)
78	Methylpyrene	2667	216 (100), 215 (45), 95 (39)
79	Methylfluoranthene or methylpyrene	2674	216 (100), 215 (70), 95 (42)
	p,p'-DDT	2762	235 (100), 165 (70), 237 (62)
80	Terphenyl	2789	230 (100), 229 (40), 101 (30)
81	Benzo[b]naphtho[2,1-d]thiophene	2822	234 (100), 129 (74), 117 (58)
82	Benzophenanthrene or benzoanthracene	2832	228 (100), 226 (87), 113 (69)
83	Benzonaphthothiophene	2848	234 (100), 117 (18), 235 (16)
84	Benzonaphthothiophene	2875	234 (100), 117 (26), 235 (17)
85	d_{12}-Chrysene (IS)	2908	240 (100), 120 (34), 239 (32)
86	Chrysene	2929	228 (100), 226 (88)
87	Methyl benzonaphthothiophene	2949	248 (100), 124 (48), 247 (36)
88	Methyl benzonaphthothiophene	2974	248 (100), 247 (37), 124 (35)
89	Methyl benzonaphthothiophene	2985	248 (100), 247 (32), 115 (25)
90	Bis(2-ethylhexyl)phthalate	3001	149 (100), 57 (48), 167 (38)
91	Methyl benzonaphthothiophene	3004	248 (100), 247 (30), 124 (23)
92	Methylbenzo[a]anthracene or	3039	242 (100), 121 (37), 120 (27)
93	Methylchrysene	3061	242 (100), 121 (89), 120 (74)
94	Methylbenzo[a]anthracene or	3074	242 (100), 120 (41), 240 (38)
95	Methylchrysene	3083	242 (100), 239 (33), 120 (24)

(continued)

TABLE 16 (continued)

GC peak No.	Tentatively identified component	Scan No.[a]	Characteristic ions in mass spectrum
96	Methylbenzo[a]anthracene or methylchrysene	3091	242 (100), 239 (30), 120 (20)
97	1,1'-Binaphthyl and 242 PAH	3102	
98	1,2'-Binaphthyl	3114	254 (100), 252 (33), 126 (28)
99	2,2'-Binaphthyl	3133	254 (100), 252 (31), 126 (25)
100	Unknown	3145	195 (100), 196 (57), 117 (44)
101	Dimethylbenzo[a]anthracene or	3186	256 (100), 239 (23), 120 (26)
102	Dimethylchrysene or	3210	256 (100), 239 (24), 120 (20)
103	Dimethyltriphenylene	3222	256 (100), 239 (22), 120 (25)
104	Dimethylbenzo[a]anthracene or	3230	256 (100), 239 (19), 120 (23)
105	Dimethylchrysene	3250	256 (100), 239 (19), 120 (23)
106	Benzofluoranthene	3271	252 (100), 126 (57), 125 (45)
107	$C_{18}H_{10}S$	3278	258 (100), 129 (45), 260 (10)
108	$C_{18}H_{10}S$	3313	258 (100), 129 (35), 260 (10)
109	Benzo[a]pyrene	3352	252 (100), 125 (64), 126 (60)
110	Perylene	3363	252 (100), 126 (40), 250 (20)
111	Methylbenzofluoran-	3403	266 (100), 132 (49), 133 (49)
112	thene or methyl-	3432	266 (100), 265 (57), 132 (40)
113	benzopyrenes	3466	266 (100), 133 (47), 265 (33)
114	Methylbenzofluoran-	3474	266 (100), 132 (46), 133 (42)
115	thenes or methyl-	3488	266 (100), 119 (51), 133 (40)
116	benzopyrene	3507	266 (100), 19 (54), 133 (51)
117	Dinaphthothiophene	3575	284 (100), 142 (42), 132 (33)
118	Dinaphthothiophene	3609	284 (100), 142 (25)
119	Benzophenanthrothiophene	3625	284 (100), 142 (37), 285 (22)
120	Anthrabenzothiophene	3638	284 (100), 142 (40), 285 (27)
121	Dibenzoanthracene or benzochrysene	3646	278 (100), 139 (50), 276 (50)
122	Dinaphthothiophene	3656	284 (100), 142 (35), 132 (30)
123	Indeno[1,2,3-cd]pyrene	3672	276 (100), 138 (62), 137 (35)
124	Dibenzo[a,h]anthracene	3680	278 (100), 139 (46), 138 (24)
125	Dibenzoanthracene or benzochrysene	3705	278 (100), 139 (42), 138 (33)
126	Dibenzoanthracene or benzochrysene	3716	278 (100), 139 (44), 138 (33)
127	Benzo[ghi]perylene	3742	276 (100), 138 (62), 137 (46)

[a] Scan speed: 1 second/scan.

TABLE 17. IDENTIFICATION OF COMPONENTS IN FRACTION IV OF THE NBS SEDIMENT EXTRACT

GC peak No.	Tentatively identified component	Scan No.[a]	Characteristic ions in mass spectrum
1	Alkane	124	57 (100), 71 (50), 85 (5)
2	Unknown	139	56 (100), 55 (55), 69 (28)
3	Styrene	157	104 (100), 58 (64), 78 (45)
4	Benzaldehyde	216	77 (100), 105 (93), 106 (84)
5	Ethylhexanol	281	57 (100), 55 (26), 56 (23)
6	1H-Indene	299	115 (100), 116 (98), 58 (17)
7	1-Phenylethanone	322	105 (100), 77 (79), 51 (32)
8	1-(2-Propenyloxy)heptane	349	58 (100), 71 (28), 55 (26)
9	d_8-Naphthalene (IS)	445	136 (100), 108 (17), 68 (25)
10	Acetic acid phenylethyl ester	662	104 (100), 66 (57), 78 (12)
11	Acenaphthylene	717	152 (100), 76 (19), 151 (18)
12	Unknown	749	116 (100), 115 (26), 117 (10)
	Acenaphthene	751	153 (100), 154 (88), 152 (78)
13	Unknown	760	116 (100), 115 (26), 117 (10)
	Fluorene	841	166 (100), 165 (96), 83 (31)
14	Unknown	918	192 (100), 190 (91), 189 (66)
15	Fluorenone	976	180 (100), 152 (43), 76 (26)
16	Phenanthrene	1010	178 (100), 179 (16), 176 (15)
17	d_{10}-Anthracene	1014	188 (100), 94 (30), 80 (28)
18	Anthracene	1018	178 (100), 179 (16), 176 (15)
19	Methylfluorenone	1037	194 (100), 165 (83), 67 (78)
20	Methylfluorenone	1047	194 (100), 165 (87), 82 (29)
21	Unknown	1059	167 (100), 181 (52), 192 (48)
22	Methyldibenzothiophene	1065	198 (100), 197 (50)
23	Methylfluorenone	1075	194 (100), 165 (96), 82 (31)
24	Methylfluorenone and methyldibenzothiophene	1084	
25	Methylanthrone	1103	208 (100), 152 (30), 178 (23)
26	Methylanthrone and di-*n*-butylphthalate	1149	208 (100), 165 (50), 178 (22)
27	Methylanthrone	1163	208 (100), 165 (48), 152 (45)
28	Sulfur	1205	64 (100), 96 (60), 128 (36)

(continued)

TABLE 17 (continued)

GC peak No.	Tentatively identified component	Scan No.	Characteristic ions in mass spectrum
29	Cyclopenta[def]phenanthrenone	1217	204 (100), 176 (39), 88 (33)
	Fluoranthene	1226	202 (100), 101 (71), 100 (40)
	Pyrene	1264	202 (100), 101 (26), 100 (17)
30	p,p'-DDD	1357	235 (100), 237 (76), 165 (73)
31	Endosulfan sulfate	1412	272 (100), 387 (15)
32	Benzofluorenone and n-butylbenzylphthalate	1429	230 (100), 101 (41), 202 (29)
33	Benzofluorenone	1449	230 (100), 202 (59), 101 (48)
34	Benzofluorenone	1467	230 (100), 202 (59), 101 (45)
35	Mthylbenzofluorenone	1487	244 (100), 215 (51), 106 (35)
36	d_{12}-Chrysene (IS)	1490	240 (100), 120 (34), 239 (30)
	Chrysene	1494	228 (100), 226 (88), 229 (19)
37	Unknown	1500	217 (100), 109 (42), 244 (16)
38	Methylbenzofluorenone	1507	244 (100), 215 (57), 95 (58)
39	Methylbenzofluorenone	1518	244 (100), 108 (47), 215 (46)
40	Benzanthracenequinone	1532	258 (100), 114 (40), 256 (35)
41	Bis(2-ethylhexyl)phthalate	1538	149 (100), 57 (48), 167 (38)
42	Benzanthracenequinone	1566	258 (100), 114 (41), 256 (39)
43	Unknown (M.W. 231)	1568	231 (100), 115 (59), 230 (42)
44	Benzanthracenequinone	1585	258 (100), 114 (36), 101 (26)
45	Benzanthracenequinone	1600	258 (100), 114 (36), 101 (26)
46	$C_{19}H_{10}O$[b]	1648	254 (100), 112 (35), 113 (30)
47	$C_{19}H_{10}O$	1663	254 (100), 112 (33), 113 (30)
	$C_{19}H_{10}O$	1674	254 (100), 113 (46), 112 (32)
	Benzo[a]pyrene	1713	252 (100), 125 (64), 126 (58)
48	Indenoanthracenone	1840	280 (100), 125 (27), 126 (25)
49	Methylcholestane	1848	55 (100), 81 (63), 280 (47)
50	Indenoanthracenone	1860	280 (100), 126 (56), 125 (54)
	Dibenzo[a,h]anthracene	1871	278 (100), 139 (46), 138 (23)
51	Indenoanthracenone	1873	280 (100), 126 (56), 125 (54)

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[a] Scan speed: 2 seconds/scan.

[b] See Table 14 for possible chemical structures.

TABLE 18. IDENTIFICATION OF COMPONENTS IN THE ACIDIC EXTRACT

GC peak No.	Compound	Scan No.[a]	Characteristic ions in mass spectrum
1	Fatty acid	126	60 (100), 73 (45), 55 (20)
2	Phenol	182	94 (100), 66 (45), 65 (30)
3	Fatty acid	188	60 (100), 73 (44), 55 (20)
4	Fatty acid	250	60 (100), 73 (47), 55 (20)
5	Benzoic acid	309	105 (100), 122 (82), 77 (82)
6	d_8-Naphthalene (IS)	314	136 (100), 108 (17), 68 (25)
7	Fatty acid	411	60 (100), 73 (92), 55 (86)
8	Fatty acid	425	60 (100), 73 (90)
9	Fatty acid	459	60 (100), 73 (90)
10	Fatty acid	464	60 (100), 73 (90)
11	Fatty acid	506	73 (100), 60 (93), 55 (80)
12	Fatty acid	511	73 (100), 60 (93)
13	Unknown	564	195 (100), 210 (46), 180 (27)
14	d_{10}-Anthracene (IS)	613	188 (100), 94 (30), 80 (28)

[a] Scan speed: 2 seconds/scan.

Consequently, no indication about the position of the substituent or the particular alkyl radical has been made. An example is given in Figure 23, which is the mass spectrum of a dimethylnaphthalene. The results of the library search are shown in Figure 24. It can be noticed that several isomers of dimethylnaphthalene were retrieved with very large FIT and PURITY indices. However, this identification was assigned only as tentative since the GC retention times for all possible dimethyl-substituted naphthalenes were not obtained.

When the number of isomers was limited, as was the case of monosubstituted naphthalenes, such as methylnaphthalene and phenylnaphthalene, the exact position was indicated after consulting the retention indices of a series of polycyclic aromatic hydrocarbons determined with an SE-52 capillary column.[7]

Total ion chromatograms of each of the four silica gel fractions are given in Figures 25 through 28. Figures 26 through 28 have also been expanded on several pages and appear again as Figures 29 through 31. For each GC peak in Figures 29 through 31 a number has been assigned that coincides with the GC peak number in the corresponding table that contains the tentatively identified components, the scan number, and the three most intense ions in the mass spectrum with their corresponding intensities.

Supplementary information with regard to the tentatively identified components in Tables 15 through 17 can be found in Appendix B, which contains extracted ion currents for many of the compounds entered in these tables.

A table containing the tentative identities of the compounds in Fraction I is not given in the report. The only compounds identified in this fraction were the three internal standards (d_8-naphthalene at Scan No. 444, d_{10}-anthracene at Scan No. 1018, and d_{12}-chrysene at Scan No. 1493), sulfur at Scan Nos. 1202 and 1221 (probably double peak), and traces of acenaphthylene (Scan No. 720), di-n-butylphthalate (Scan No. 1153), and bis(2-ethylhexyl)phthalate (Scan No. 1539). Searches have been made for ions at m/e 57, 71, 85, and 95, characteristic for aliphatic hydrocarbons (see Appendix B, separate volume). The data indicate the presence of these aliphatics in the sample; however, since they could not be resolved from the background material, tentative identifications could not be provided.

The GC/MS analyses of the acidic extracts resulted in the tentative identification of a series of fatty acids, phenol, and benzoic acid (see Table 18 and Figure 32). Phenol was subsequently confirmed in the sample extracts by comparison of the GC retention times of the tentatively identified compound and that of the authentic standard. No attempt was made to identify the various fatty acids, either as parent compound or as methyl esters.

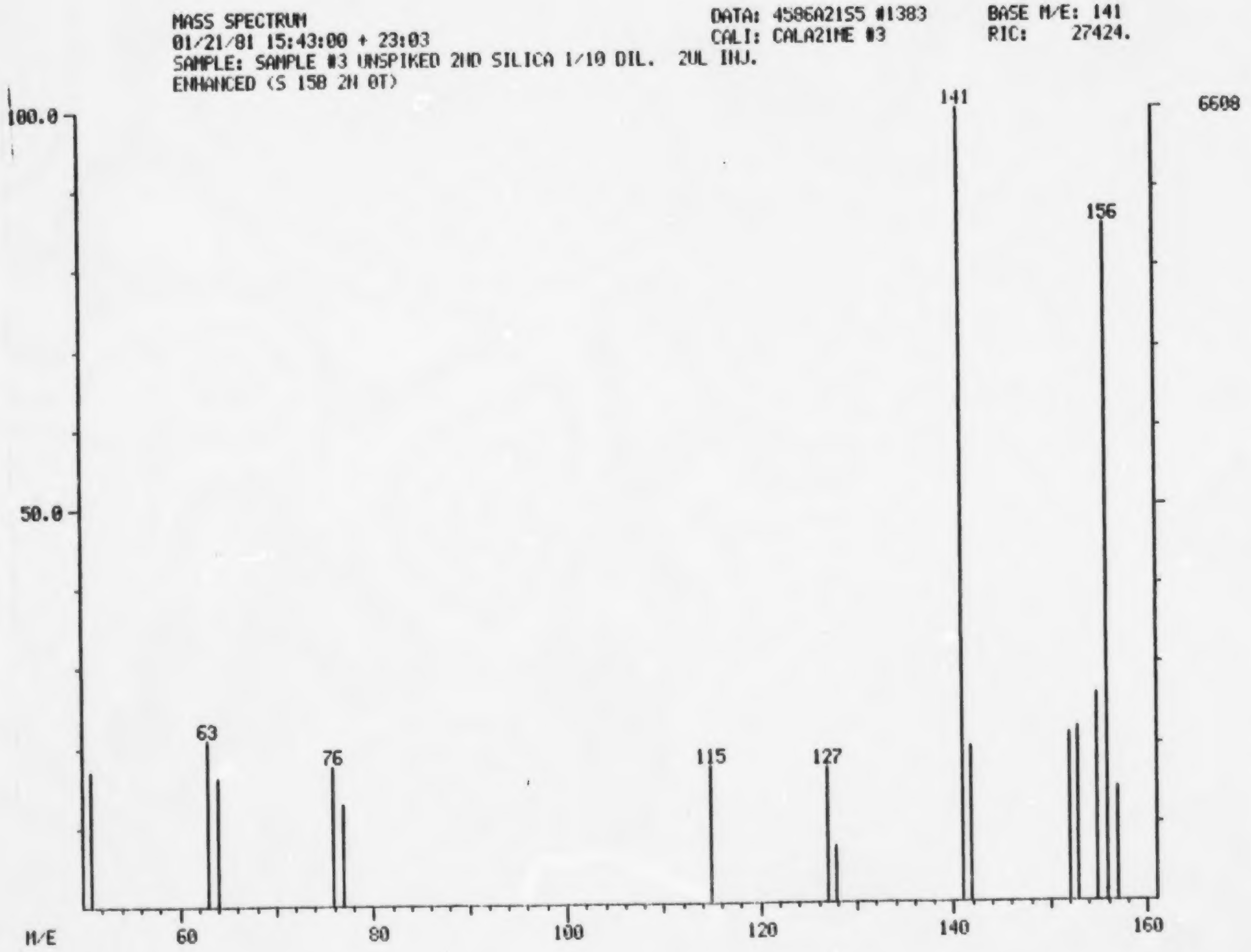

Figure 23. Electron impact mass spectrum of dimethylnaphthalene.

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LIBRARY SEARCH                       DATA: 4586A2155 #1383      BASE M/E:  141
01/21/81 15:43:00 + 23:03            CALI: CALA21ME #   3       RIC:     27423
SAMPLE: SAMPLE #3 UNSPIKED 2ND SILICA 1/10 DIL.  2UL INJ.
ENHANCED (S 15B 2N OT)

25409 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
   95 MATCHED AT LEAST 5 OF THE 15 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1   2984 NAPHTHALENE, 1, 2-DIMETHYL-
2   2981 NAPHTHALENE, 1, 4-DIMETHYL-
3   3021 NAPHTHALENE, 2, 3-DIMETHYL-
4   2989 NAPHTHALENE, 1, 3-DIMETHYL-
5   2972 NAPHTHALENE, 1, 8-DIMETHYL-

RANK  FORMULA                                        M.WT B.PK   PURITY    FIT   RFIT
1 C12.H12                                             156  156      916    916    973
2 C12.H12                                             156  156      907    907    967
3 C12.H12                                             156  156      906    906    965
4 C12.H12                                             156  156      903    903    965
5 C12.H12                                             156  156      898    898    975

MASS    INTEN      1      2      3      4      5
  51      170    136    166    127    144    141
  62                                           45
  63      210    130    138    137    141    150
  64      163    111     96    134    139     86
  76      176    223    197    231    200    220
  77      128    189    210    166    188    193
  78             126    107    133    145     71
  89                                           42
 115      173    199    173    190    187    187
 127      169     69     79     79     82     72
 128       71    119    136    144    148    136
 129              52     60     63     69     68
 139              66     51     64     65     68
 141     1000   1044    990    843    850    874
 142      197    128    100    104    105     97
 151                     33                   47
 152      212    108    101    100     93    135
 153      220    111    101    105    109    174
 154              48     42     44     46     47
 155      262    215    252    284    278    284
 156      852   1088   1128   1177   1187   1120
 157      143    141    133    165    157    139
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Figure 24. Library search for compound at scan no. 1383 in fraction II.

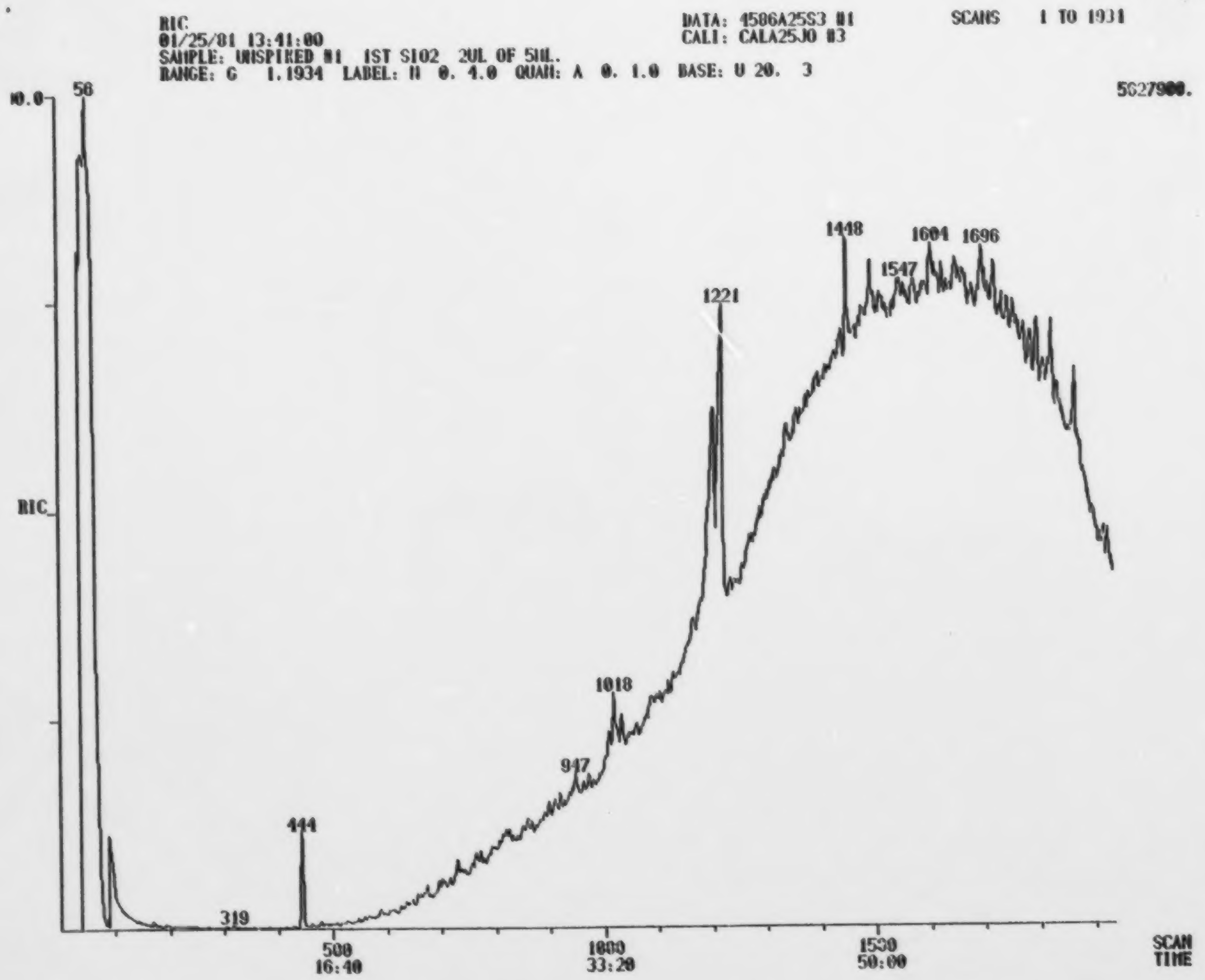

Figure 25. Capillary GC/MS chromatogram of fraction I obtained by silica gel cleanup/fractionation of the NBS sediment extract.

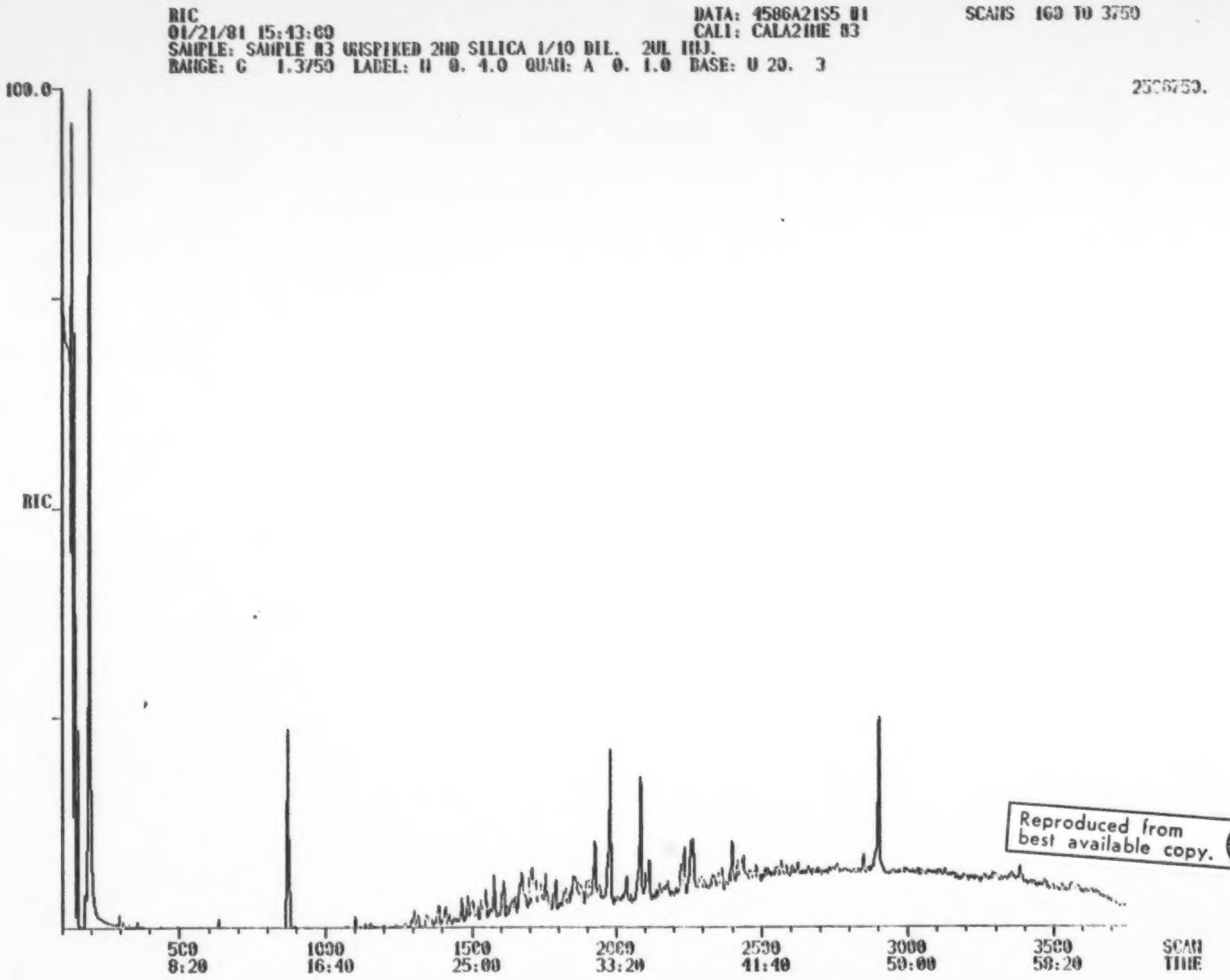

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Figure 26. Capillary GC/MS chromatogram of fraction II obtained by silica gel cleanup/fractionation of the NBS sediment extract.

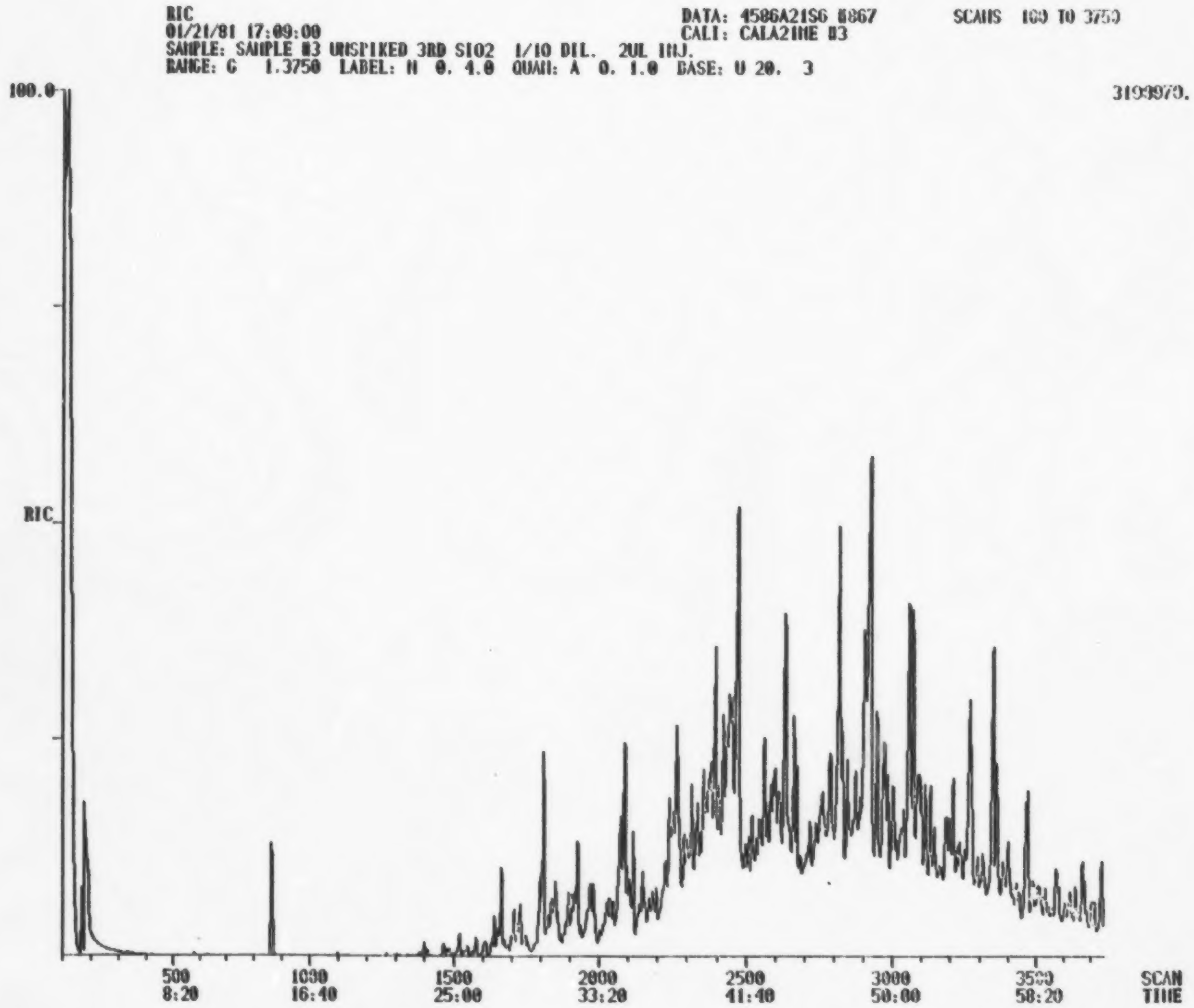

Figure 27. Capillary GC/MS chromatogram of fraction III obtained by silica gel cleanup/fractionation of the NBS sediment extract.

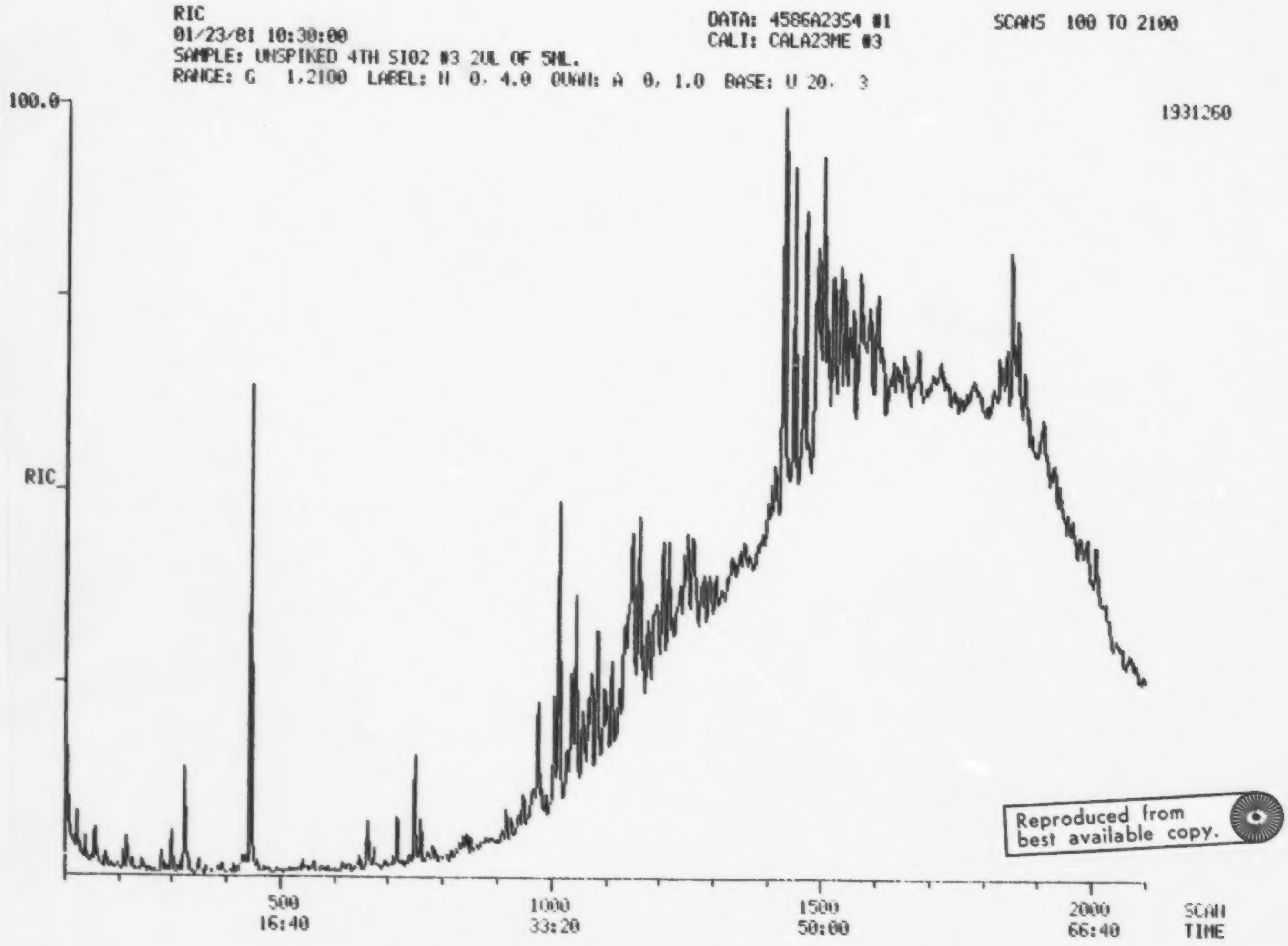

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Figure 28. Capillary GC/MS chromatogram of fraction IV obtained by silica gel cleanup/fractionation of the NBS sediment extract.

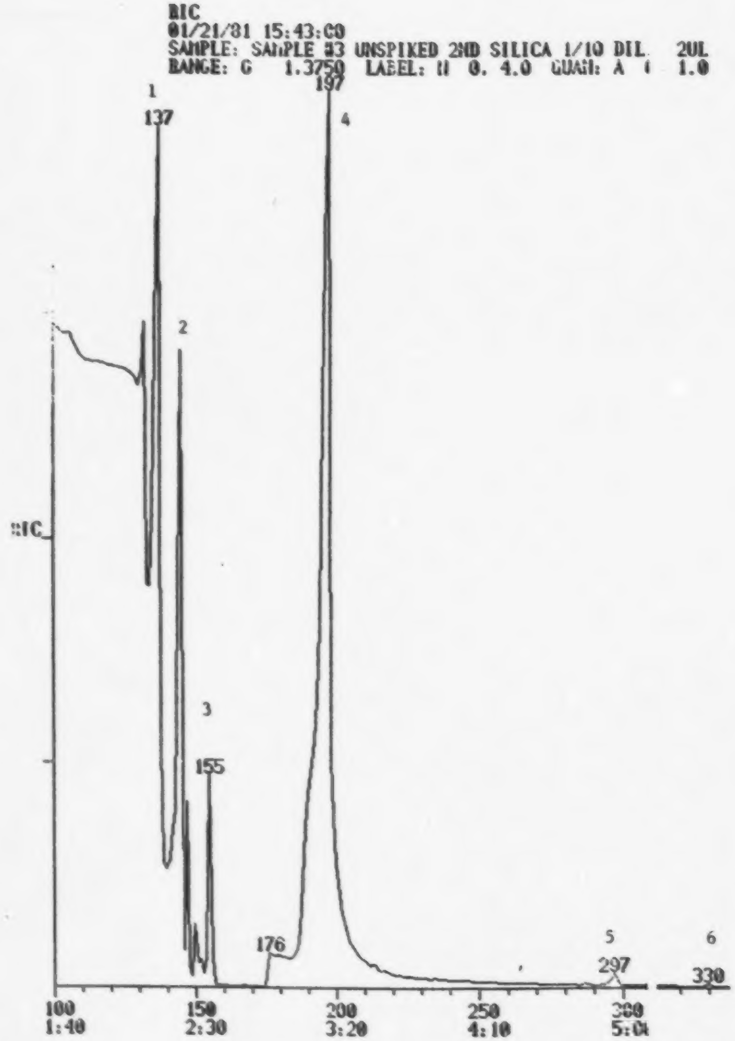


Figure 29. Expanded capillary GC/MS chromatogram of fraction II obtained by cleanup/fractionation of the NBS sediment extract.

(continued)

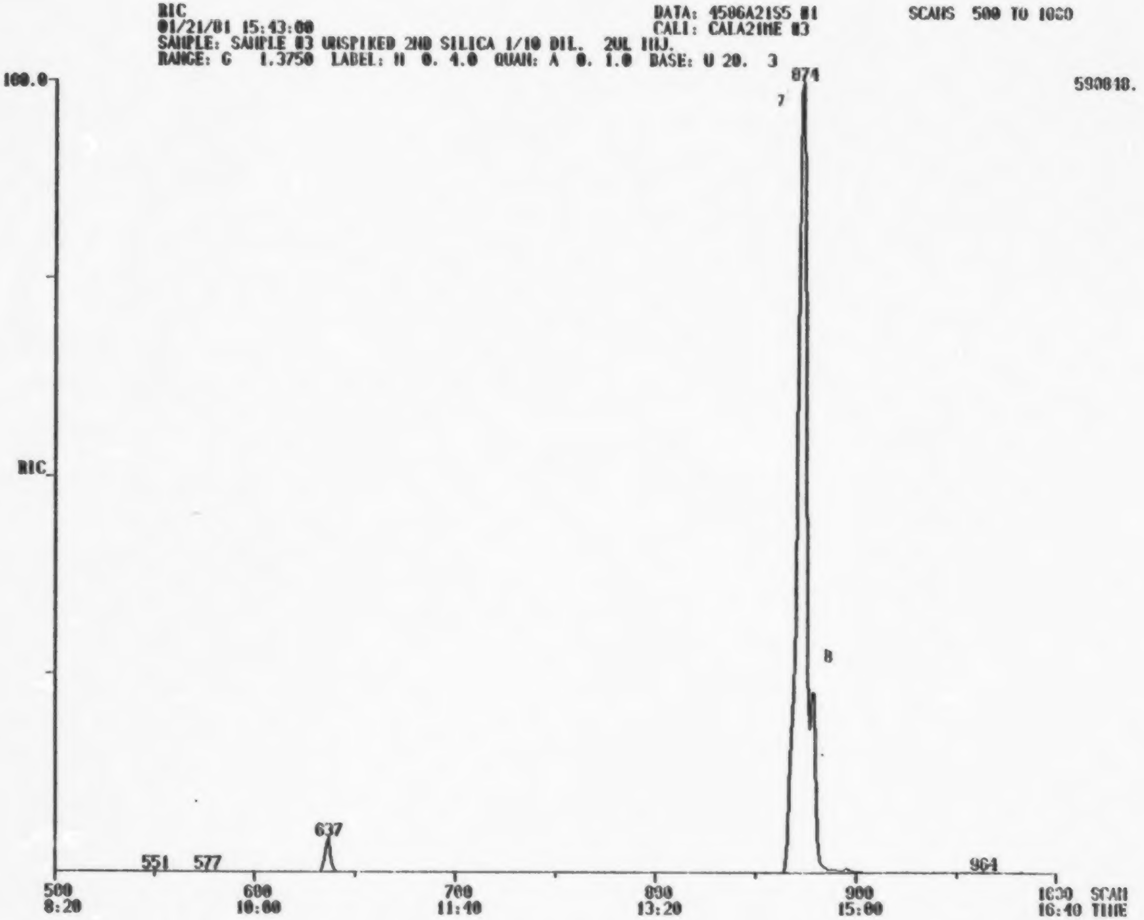
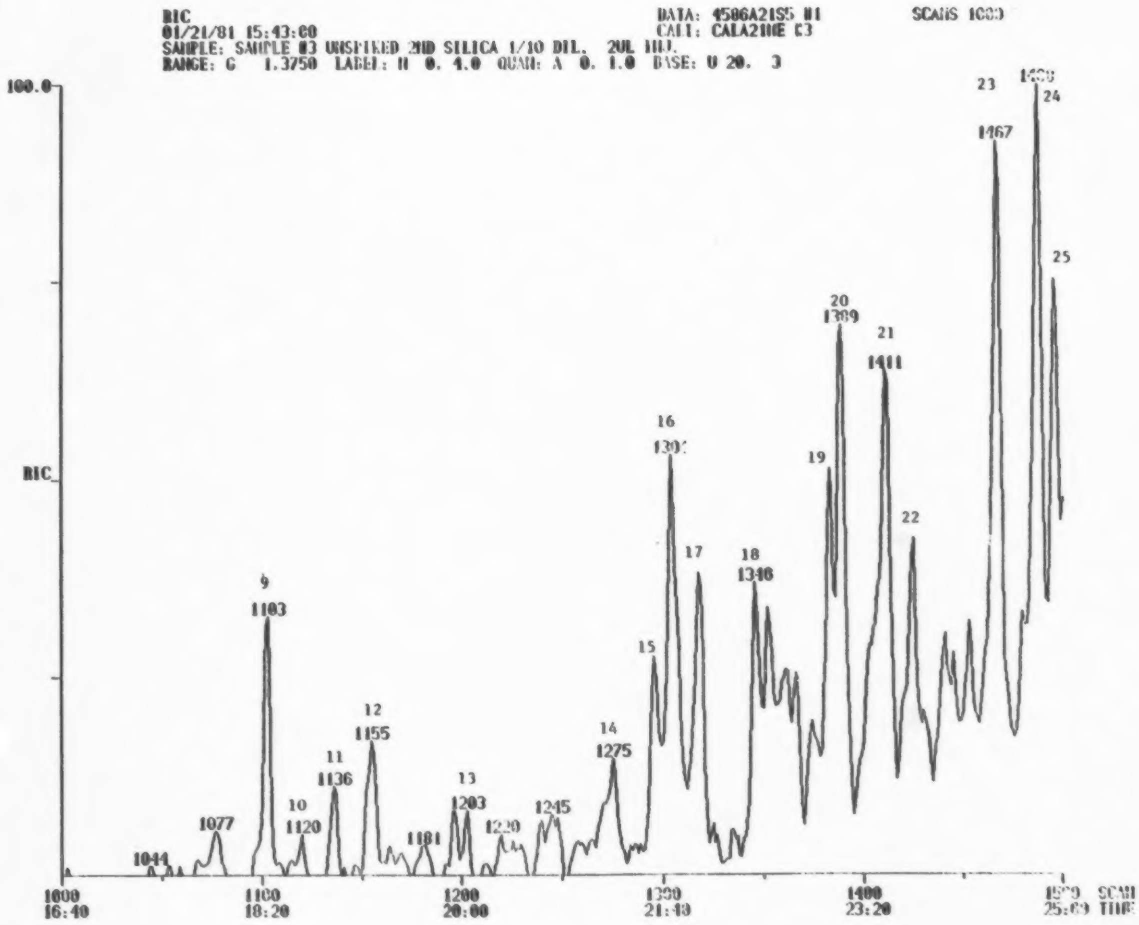


Figure 29 (continued)



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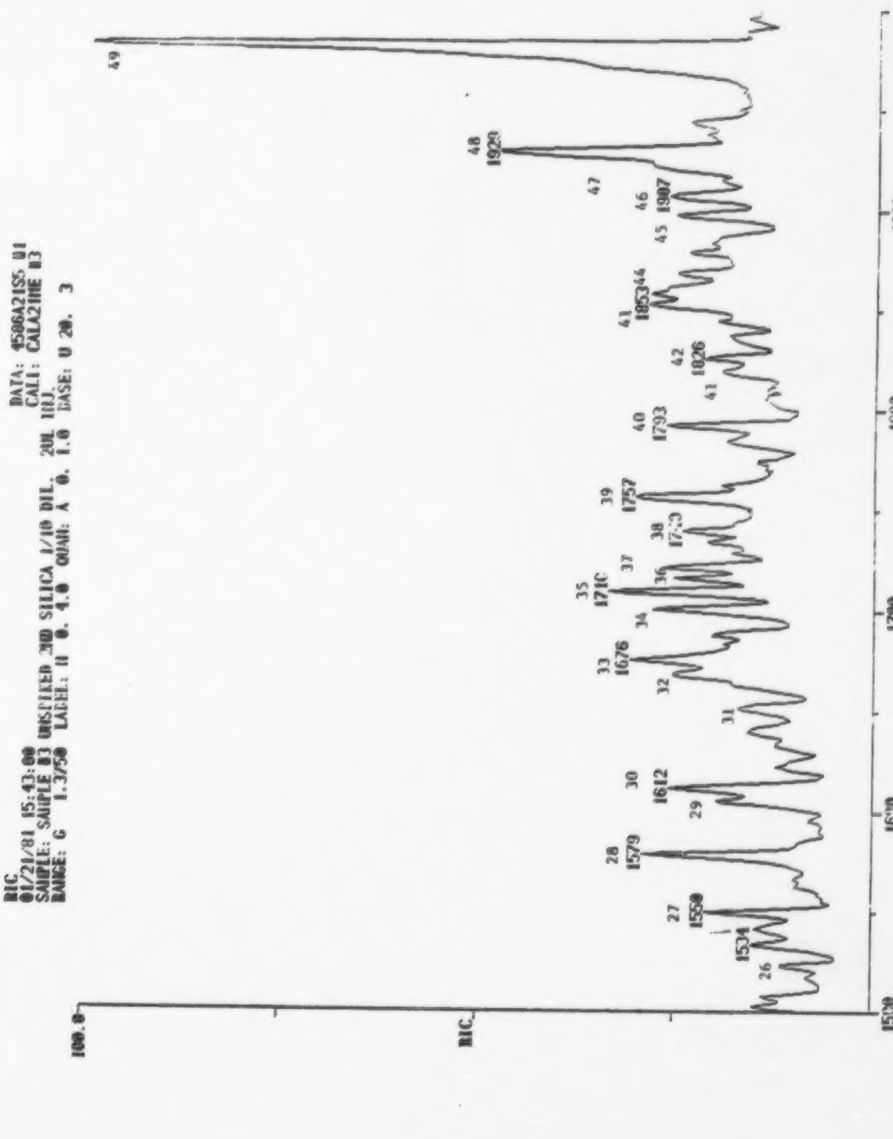

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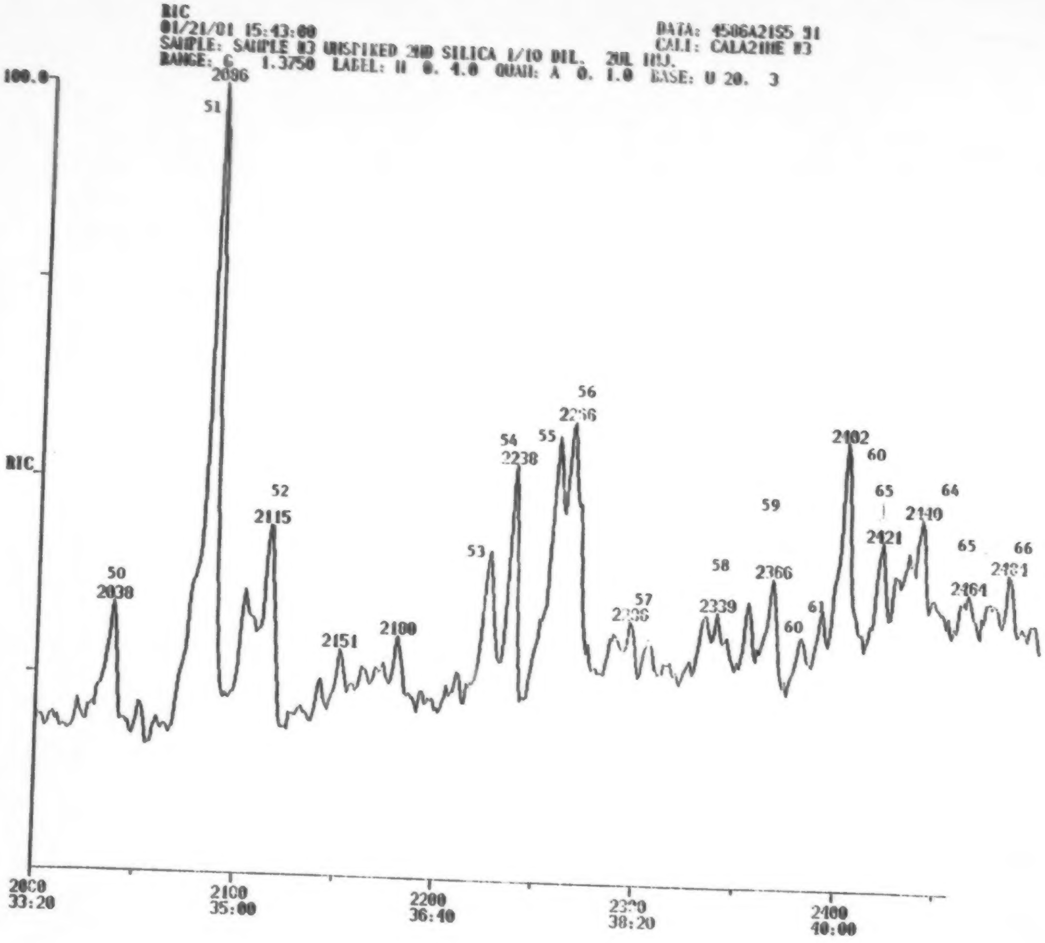
Figure 29 (continued)



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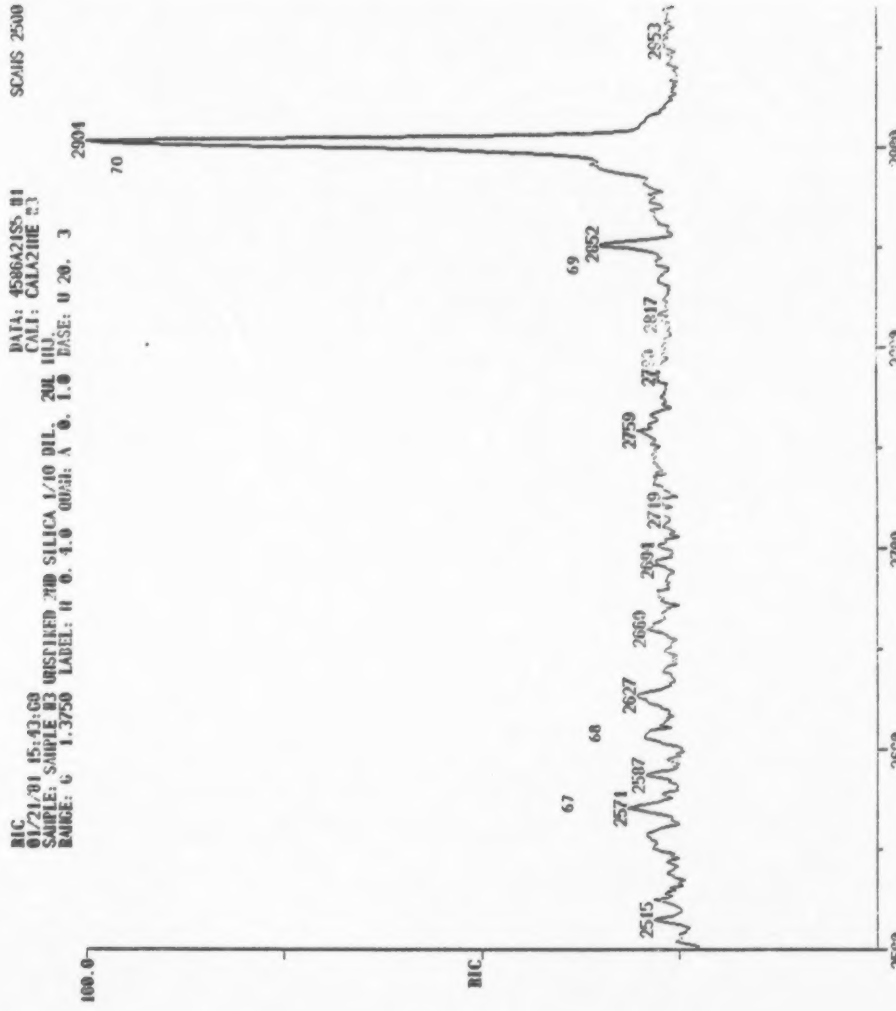

Figure 29 (continued)

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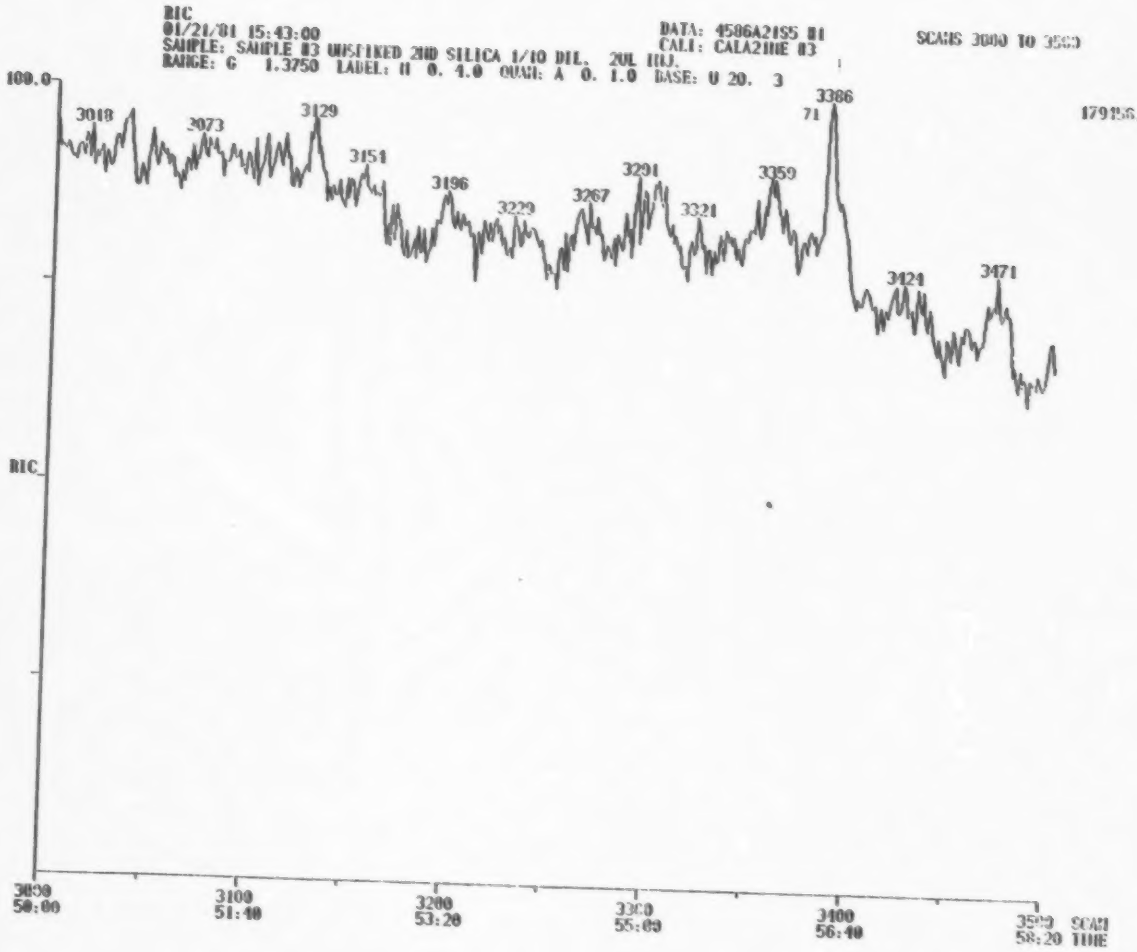

Figure 29 (continued)

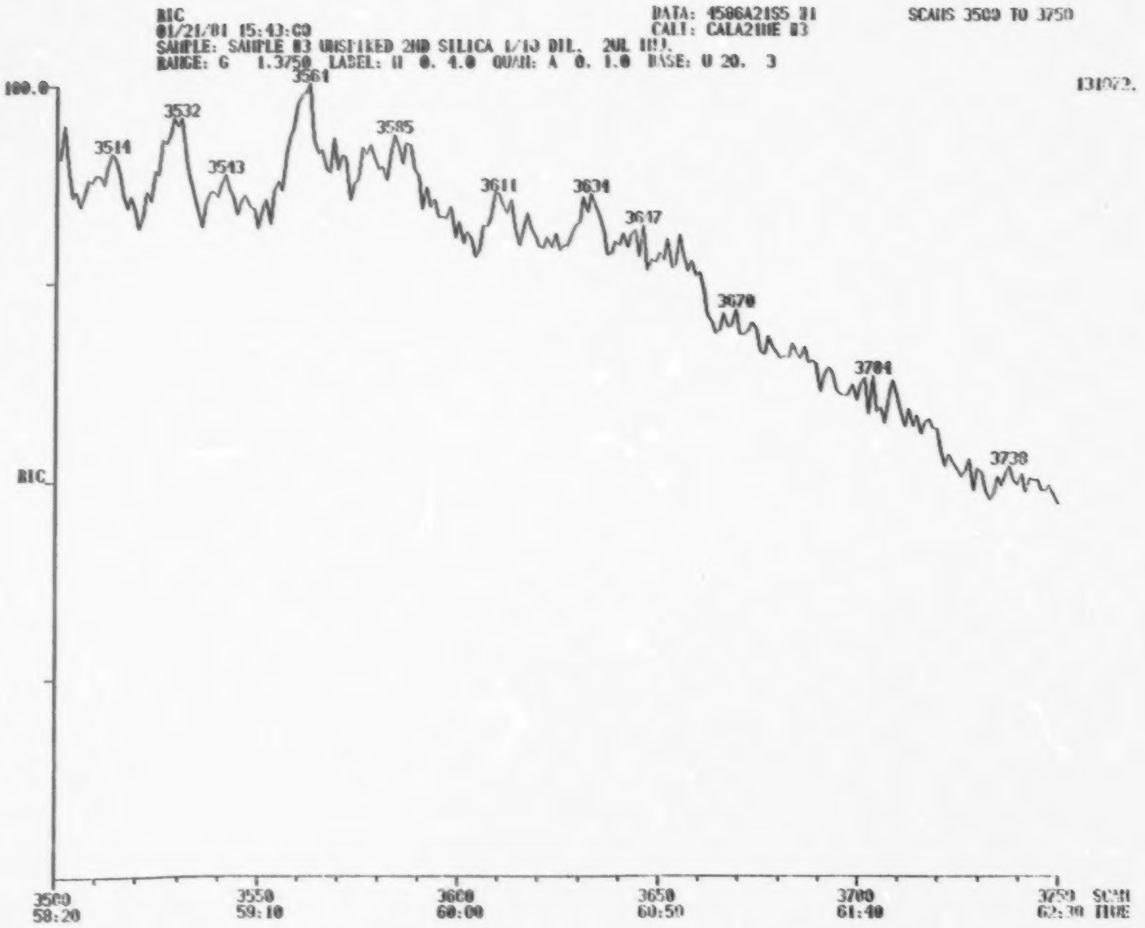

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Figure 29 (continued)

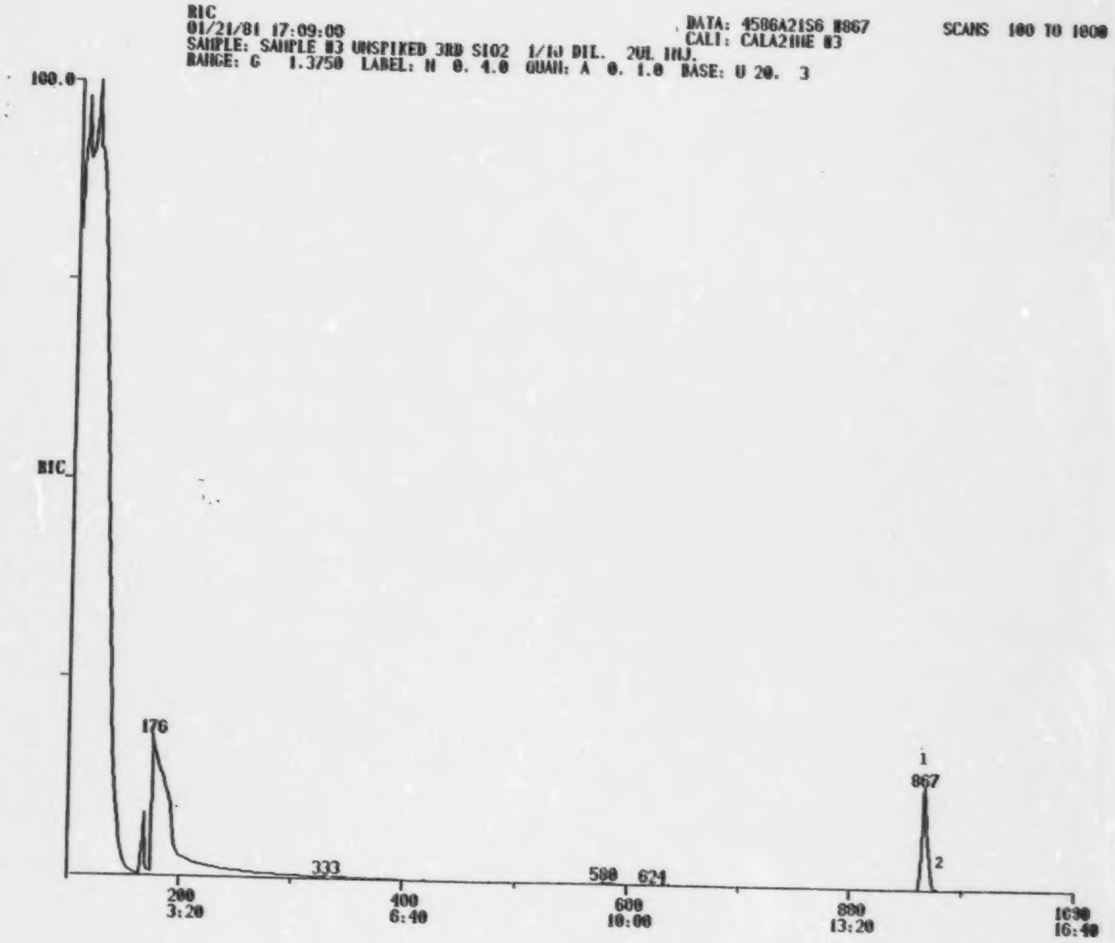
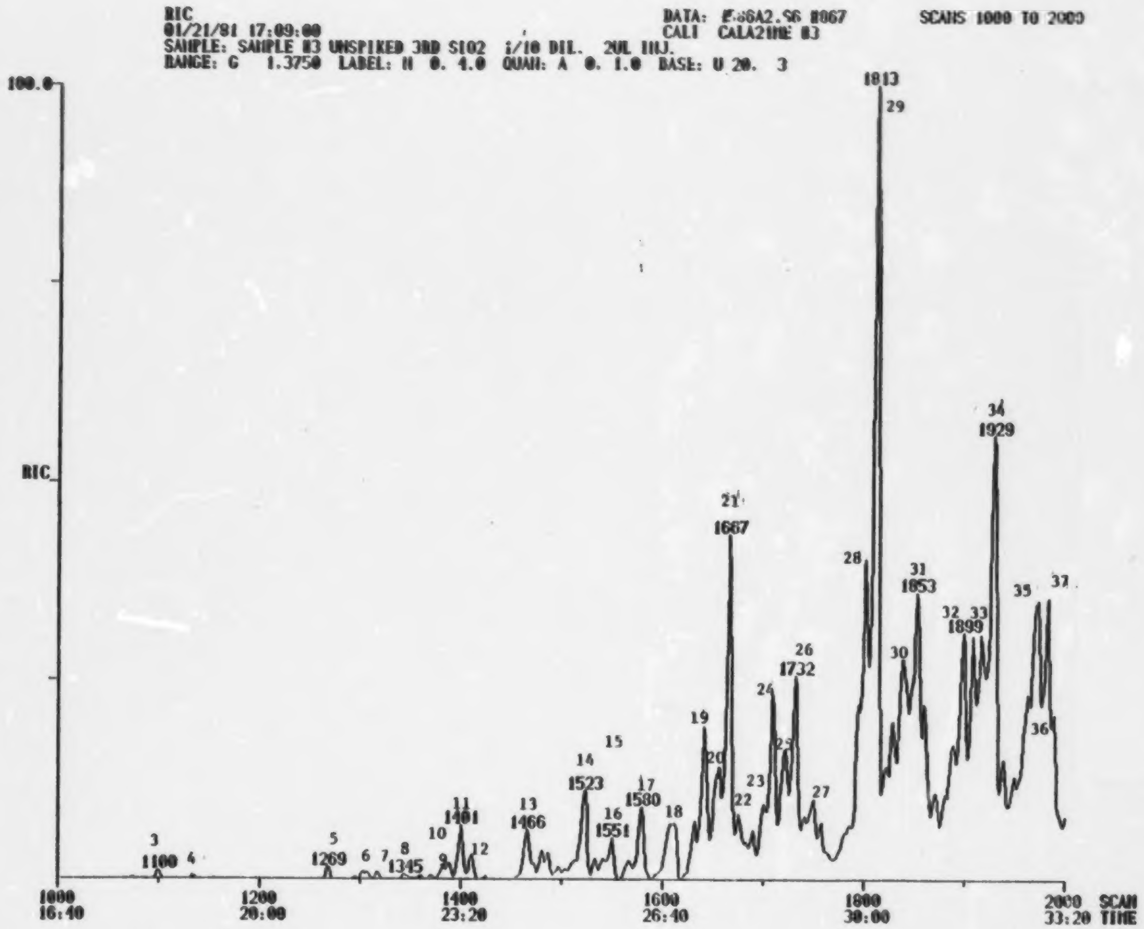


Figure 30. Expanded capillary GC/MS chromatogram of fraction III obtained by cleanup/fractionation of the NBS sediment extract.

(continued)



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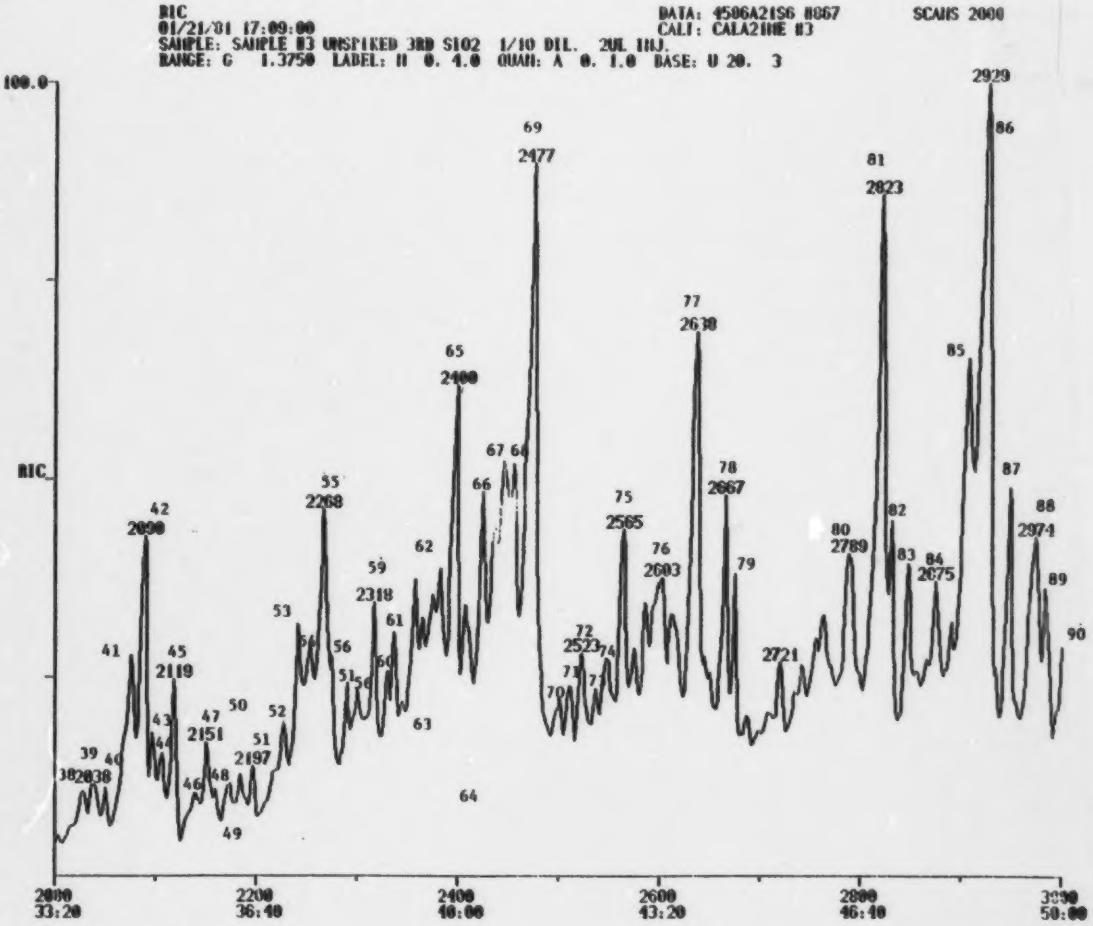

Figure 30 (continued)

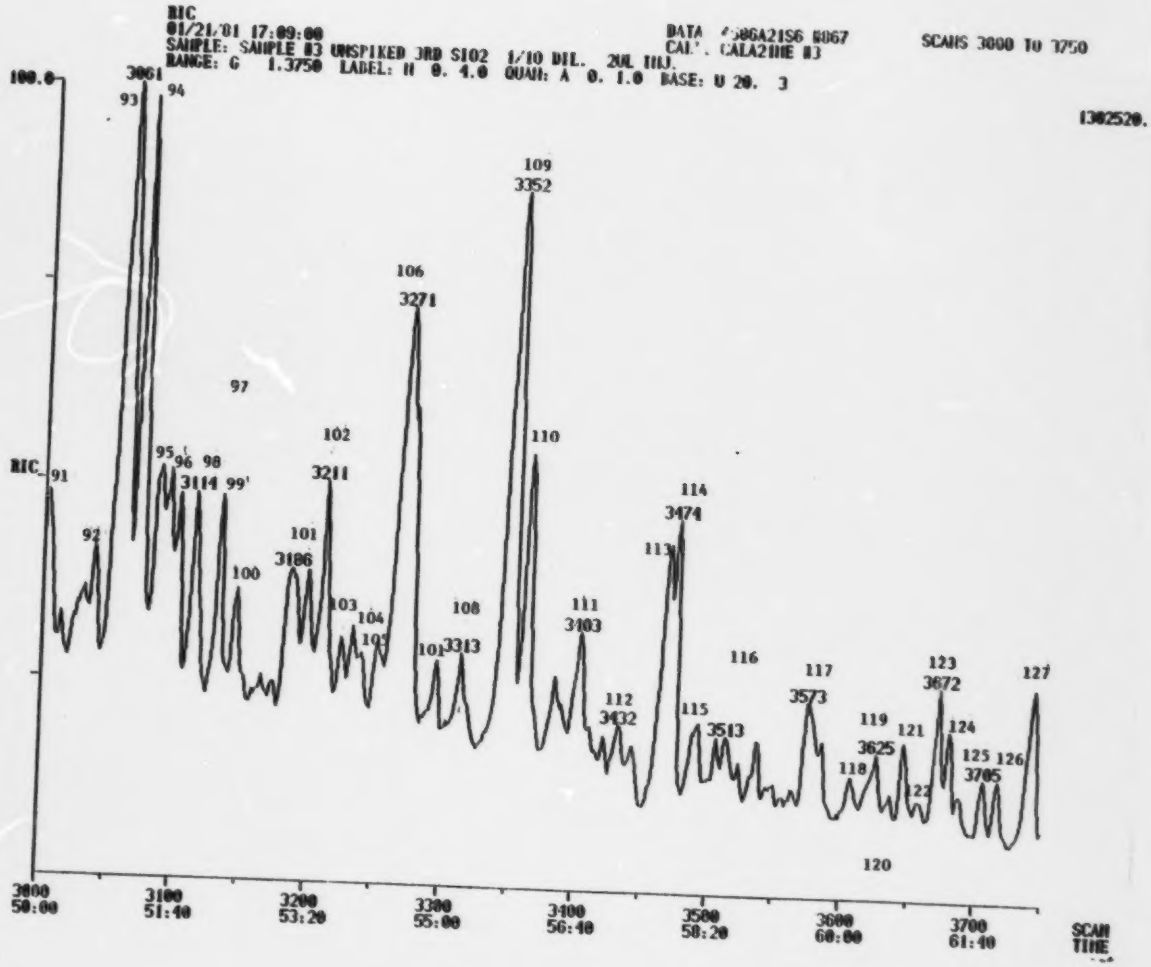

Figure 30 (continued)

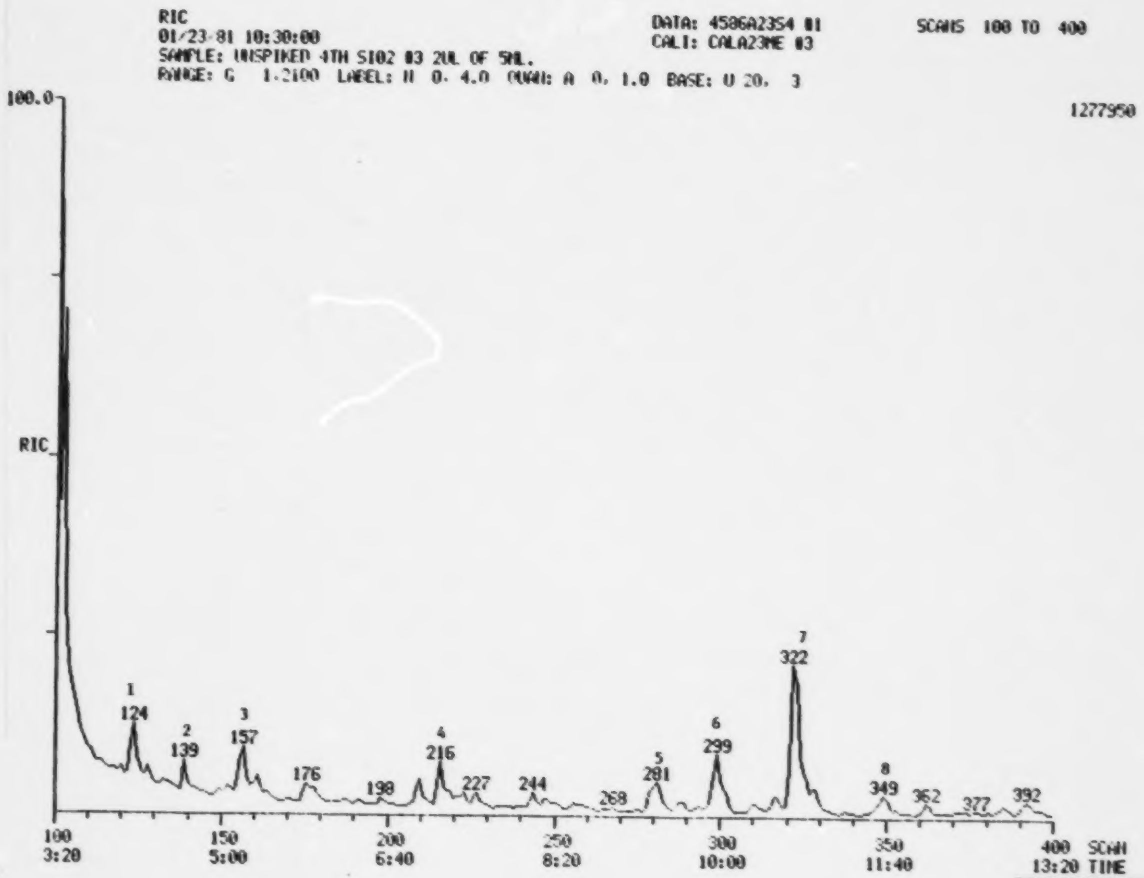

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Figure 31. Expanded capillary GC/MS chromatogram of fraction IV obtained by cleanup/fractionation of the NBS sediment extract.

(continued)

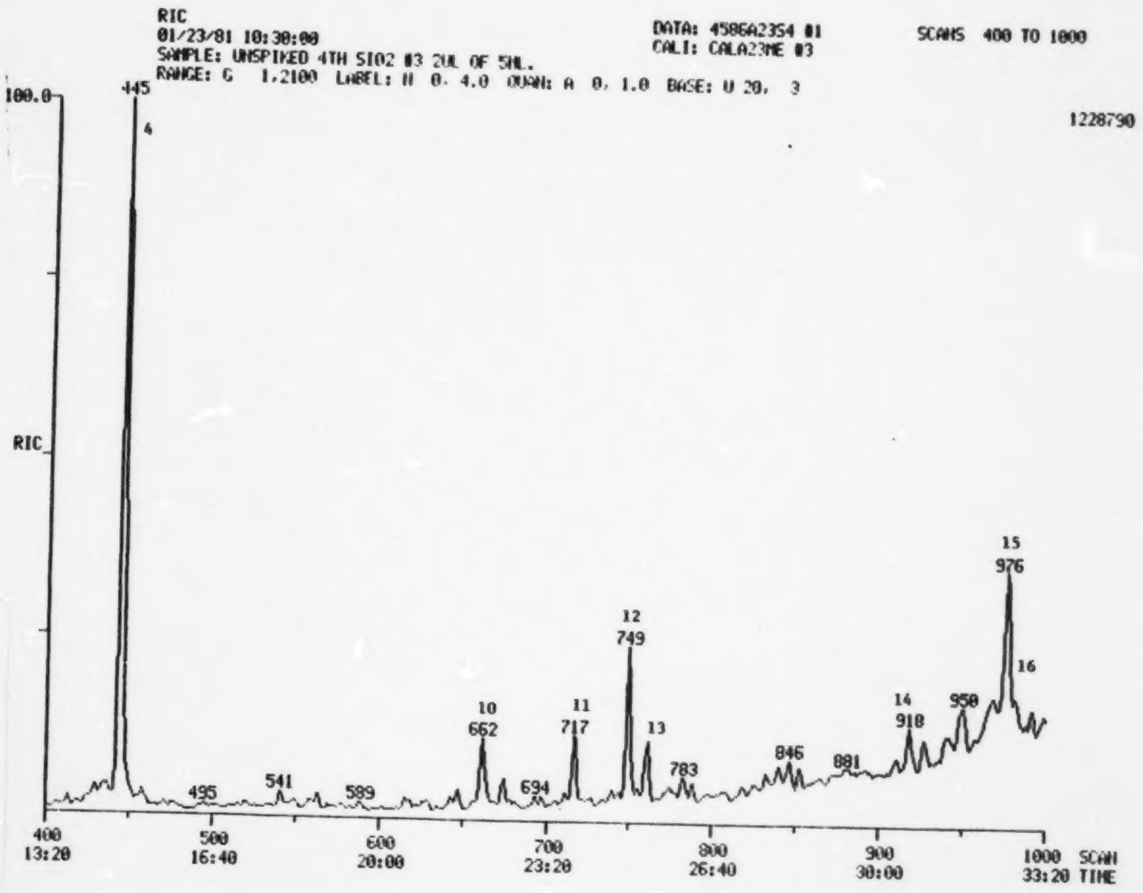

Figure 31 (continued)

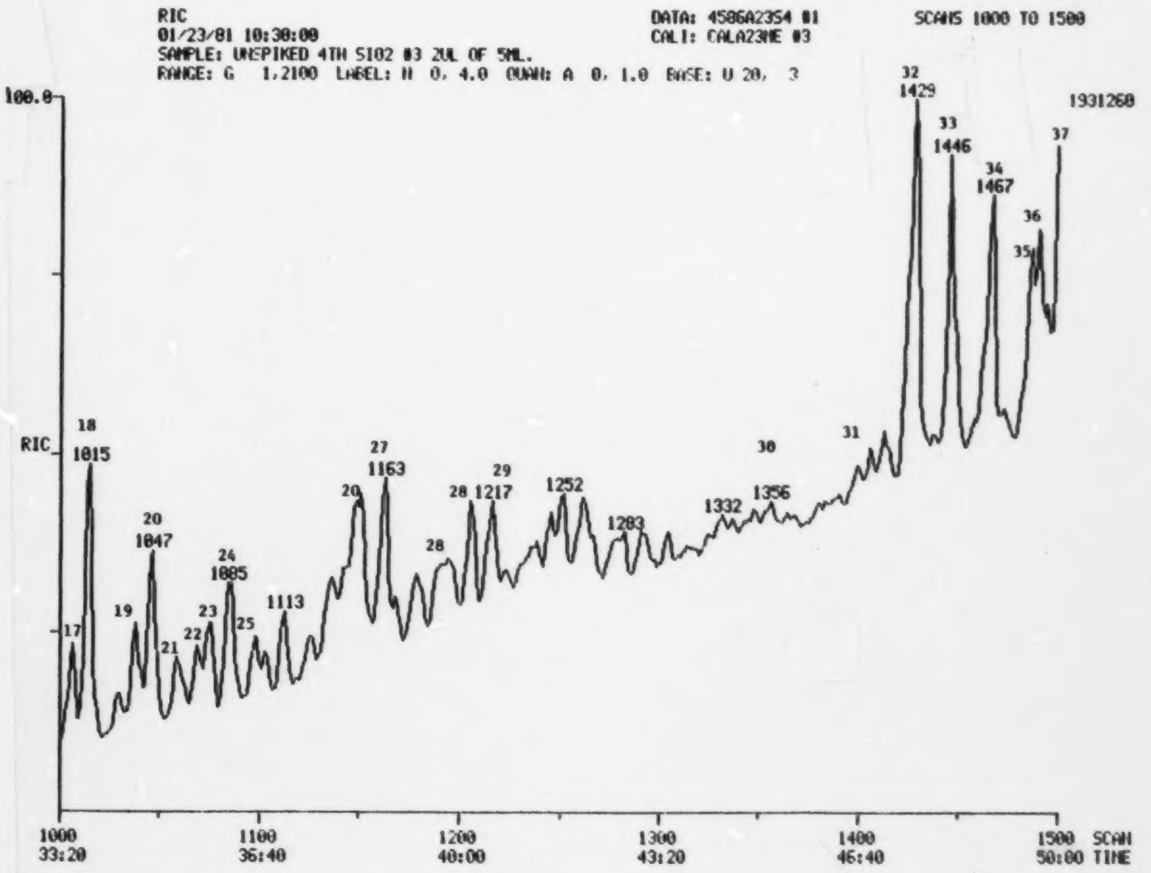

Figure 31 (continued)

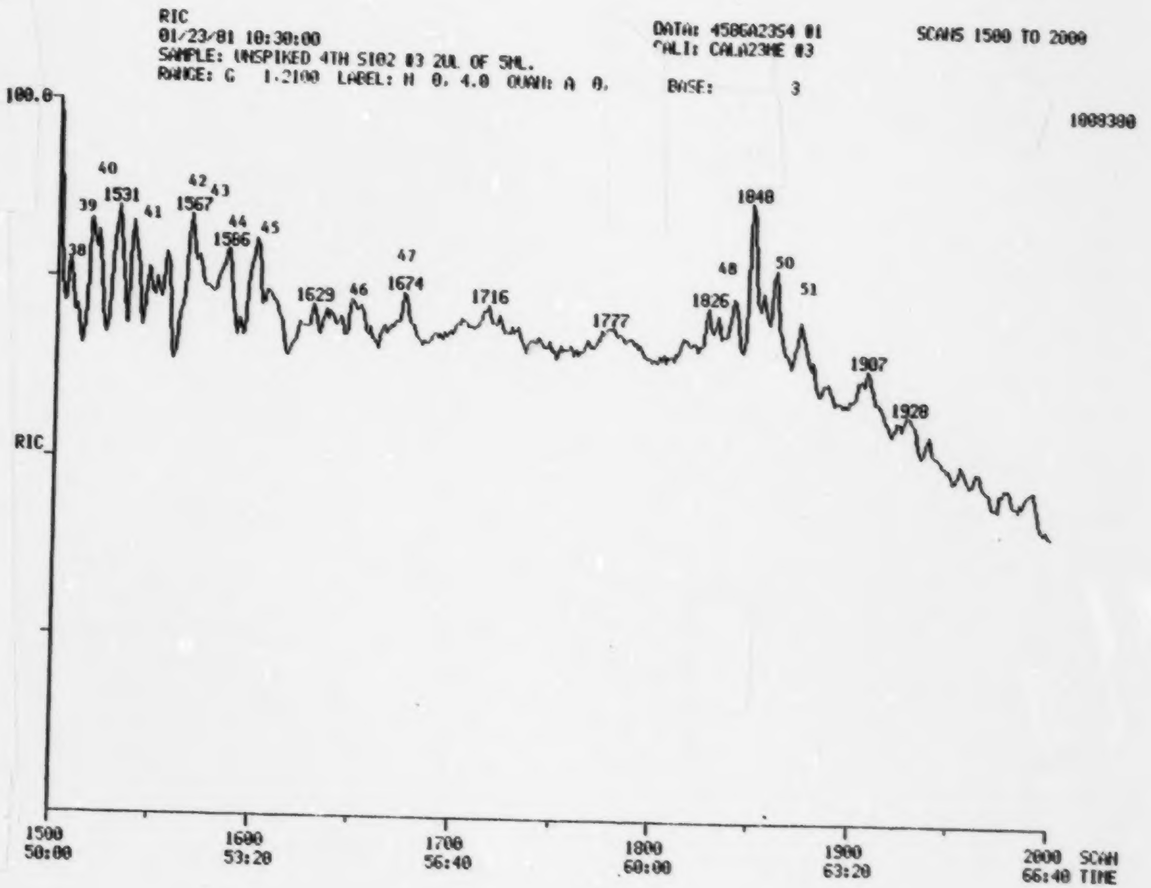

Figure 31 (continued)

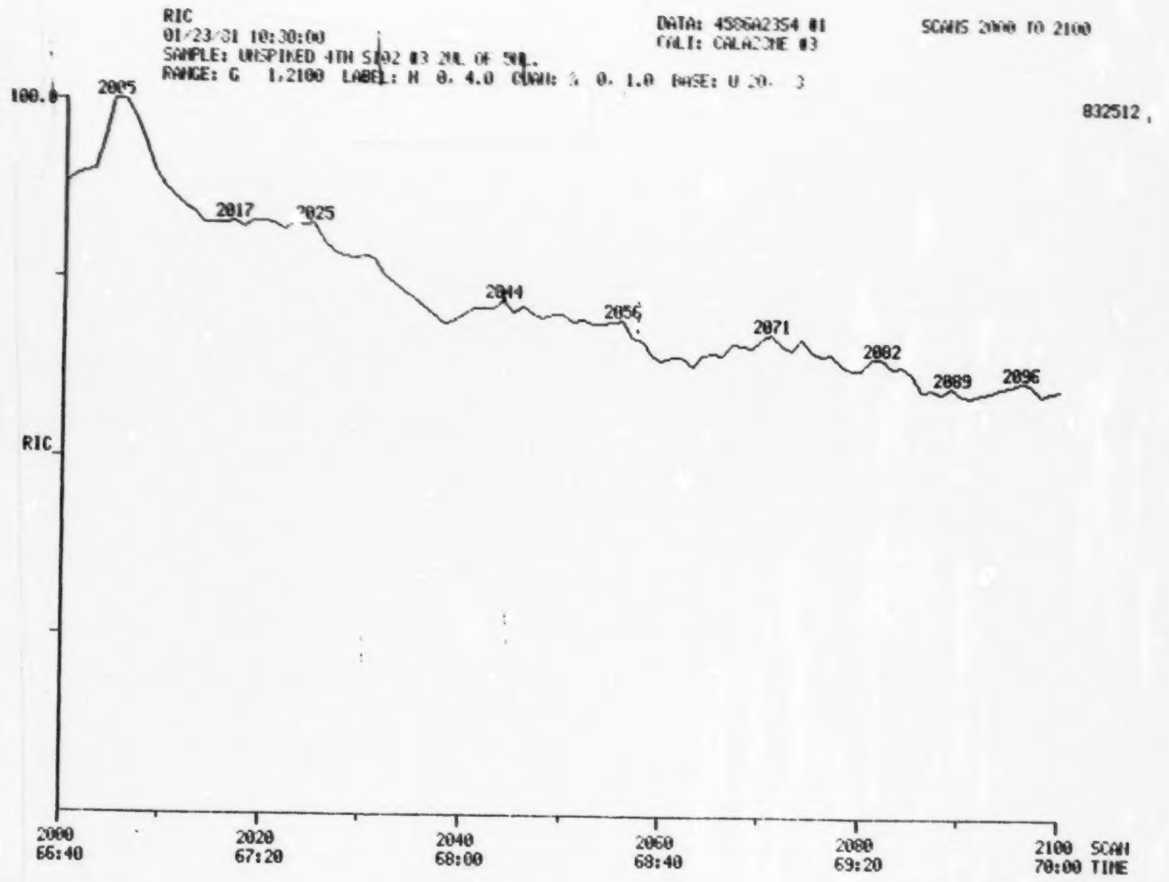

Figure 31 (continued)

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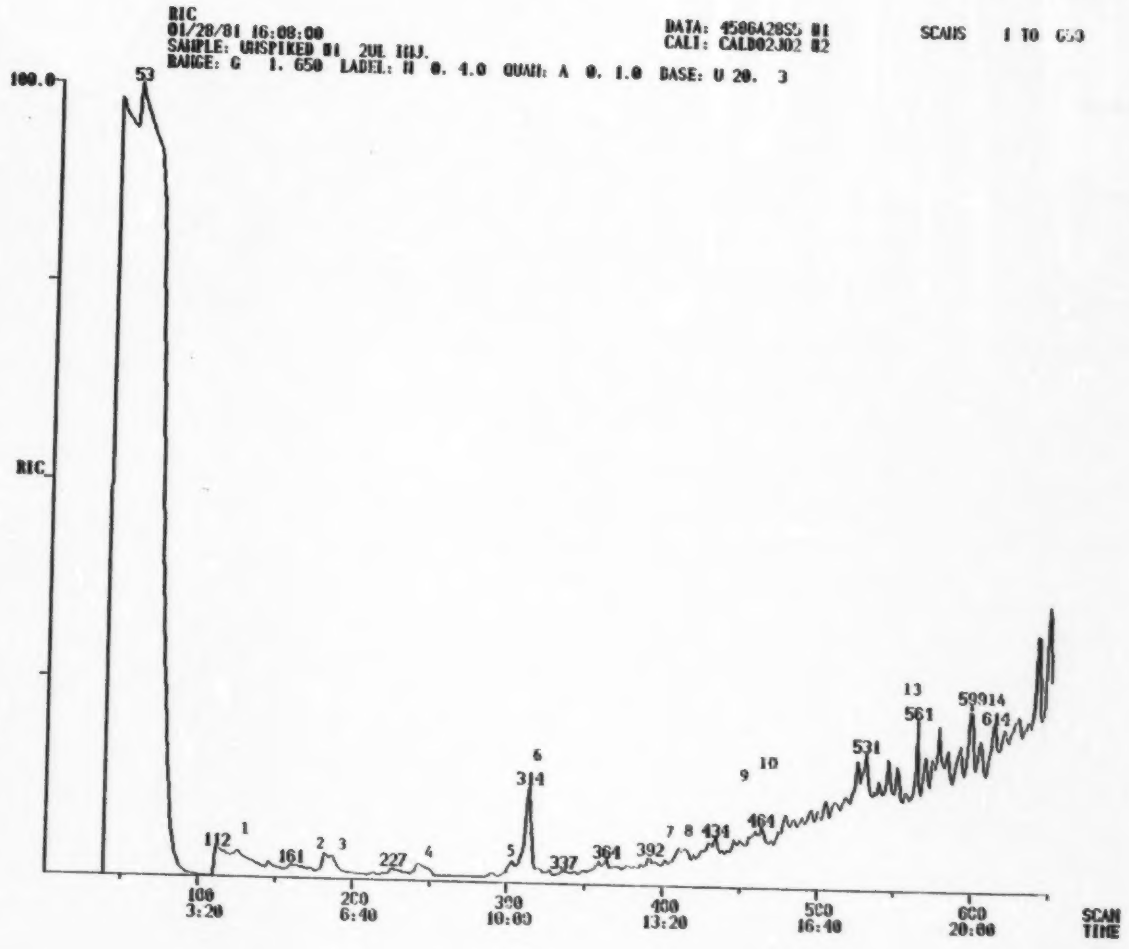

Figure 32. Capillary GC/MS chromatogram of the acidic NBS sediment extract.

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APPENDIX

PROTOCOL FOR THE ANALYSIS OF EXTRACTABLE ORGANIC PRIORITY POLLUTANTS IN INDUSTRIAL AND MUNICIPAL WASTEWATER TREATMENT SLUDGE

PROTOCOL FOR THE ANALYSIS OF EXTRACTABLE ORGANIC PRIORITY POLLUTANTS IN INDUSTRIAL AND MUNICIPAL WASTEWATER TREATMENT SLUDGE

1. Scope and Application

1.1 This method is used for the determination of the base, neutral, and acid-extractable organic compounds listed in Table 1.

1.2 The method is for qualitative and quantitative analysis of these compounds in municipal and industrial wastewater treatment sludges. The procedure requires the use of a gas chromatograph/mass spectrometer (GC/MS) as the final detector.

1.3 The method detection limit for each compound is dependent on the compound characteristics and the particular sludge analyzed. However, typical detection limits are 200 to 300 µg/liter for publicly owned treatment works (POTW) sludges with 1 to 5% total solids.

1.4 This method is restricted to use by or under the close supervision of experienced analysts. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.

2. Summary of Method

This method (Figure 1) uses repetitive solvent extraction aided by a high-speed homogenizer. The extract is separated by centrifugation and removed with a pipette or syringe. Sludges are extracted at $pH \geqq 11$ to isolate base/neutral compounds and at $pH \leqq 2$ to isolate acidic compounds. Extracts containing base/neutral compounds are cleaned by silica gel or florisil chromatography or by gel permeation chromatography (GPC). Extracts containing the acidic compounds are cleaned by GPC. The organic priority pollutants are determined in the cleaned extracts by capillary column or packed column GC/MS. Option A is preferred since capillary GC/MS (HRGC/MS) allows easier data interpretation. Qualitative identification of compounds is performed using the retention time and the relative abundance of three characteristic ions. Quantitative analysis is performed using external or internal standard techniques with a single characteristic ion.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in GC/MS chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.4.

3.1.1 Glassware must be scrupulously cleaned. All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water and reagent water. It should then be drained dry, and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality dichloromethane may be substituted for the muffle furnace heating. Volumetric glassware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. It should be stored inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the wastewater treatment system being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve acceptable detection limits.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mamalian carcinogens; benzo[a]anthracene, benzidine, 3,3'-dichlorobenzidine, benzo[a]pyrene, α-BHC, β-BHC, δ-BHC, γ-BHC, dibenzo[a,h]anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls.

5. Apparatus and Materials

5.1 Sampling, Extraction, and Extract Cleanup

5.1.1 Emulsifier-Tekmar Tissumizer® or equivalent, high capacity.

5.1.2 Centrifuge, capable of handling 200 ml bottles.

5.1.3 Centrifuge bottles with TFE lined screw caps, 200 ml.

5.1.4 Kuderna-Danish (K-D) glassware.

5.1.4.1 Snyder columns, 3 bulb, macro.

5.1.4.2 Snyder columns modified micro.

5.1.4.3 Evaporating flasks, 500 ml, 250 ml.

5.1.4.4 Receiver ampuls 5 and 10 ml, graduated, with spring attachment.

5.1.4.5 Beakers, 100 ml.

5.1.5 Water or steam bath for Kuderna-Danish concentrations.

5.1.6 Chromatographic (drying) Column - Pyrex (400 mm x 20 mm ID) without a fritted plate.

5.1.7 Separatory funnels, 500 ml with TFE stopcock.

5.1.8 Syringe, 100 ml, Pyrex, with long needle.

5.1.9 Graduated cylinder, 100 or 250 ml.

5.1.10 Vials, 2 ml, 4 ml, and 8 ml with TFE lined screw caps.

5.1.11 Sample bottles, 1,000 ml or 4,000 ml glass with TFE lined screw caps.

5.1.12 Disposable pipettes, for transferring extracts.

5.1.13 Gel Permeation Chromatograph (GPC), Analytical Biochemical Labs, Inc., GPC Autoprep 1002 or equivalent including:

5.1.13.1 Glass column 25 mm ID x 60-70 mm packed with 70 g of Bio-Beads SX-3.

5.1.13.2 Chromatographic pump, operated at 5 ml/min with 350-700 millibars (5-10 psi).

5.1.13.3 Injector with loop.

5.1.13.4 Syringe filter holder, stainless steel and TFE, Gelman 4310 or equivalent.

5.1.13.5 Spectrophotometric chromatographic detector, 254 nm, with strip chart recorder (optional, for GPC calibration).

5.1.14 Chromatographic column, 200 mm x 20 mm ID, with solvent reservoir (250 ml) and TFE stopcock.

5.1.15 Roller mill.

5.1.16 Bottles, 500 ml, brown glass.

5.2 For Identification and Quantitation

5.2.1 Gas chromatograph/mass spectrometer with data system, Finnigan 4000 or equivalent. The GC/MS interface should include a glass jet separator and a direct capillary line. The computer system should allow acquisition and storage of repetitive scan data throughout the GC/MS runs. Computer software should be available to allow searching of GC/MS data for display of extracted ion current profiles (EICPs) and integration of the peaks. The GC should have injectors for both packed columns and a splitless Grob-type capillary injector. GC columns required are:

5.2.1.1 0.9 to 1.8 m x 2 mm ID glass packed with 1% SP-1240-DA on 100/120 mesh Supelcoport.

5.2.1.2 15-30 m x 0.2 mm ID wall coated open tubular capillary column coated with SE-54 providing at least 25,000 effective theoretical plates, measured at C_{13}, or a 1.8 m x 2 mm ID glass packed with 3% SP-2250 on 100/120 mesh Supelcoport.

5.2.2 Gas chromatograph/flame ionization detector with the same GC columns as for the GC/MS system.

6. Reagents

6.1 For Extraction and Extract Cleanup

6.1.1 Dichloromethane, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.2 Hexane, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.3 Acetone, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.4 Hydrochloric acid solution (6N). Slowly add 100 ml of HCl (12N) to 100 ml of reagent water.

6.1.5 Sodium hydroxide solution (6N). Dissolve 24 g NaOH in reagent water and dilute to 100 ml.

6.1.6 Sodium sulfate (Na_2SO_4), Anhydrous, granular. Clean by overnight Soxhlet extraction with dichloromethane, drying in an oven at 110 to 160°C oven, and then heating to 650°C for 2 hr. Store in a glass jar tightly sealed with TFE-lined screw cap.

6.1.7 Silica gel, 75/150 mesh. Clean silica gel for 16 hr by Soxhlet extraction with dichloromethane. Dry and activate for 16 hr at 160°C. Deactivate by adding 3% water (by weight) and mixing for at least 4 hr on a tumbler. Store at room temperature in glass jars fitted with TFE lined screw caps.

6.1.8 Florisil 60/100 mesh, Floridan. Clean florisil for 16 hr by Soxhlet extraction with dichloromethane. Dry and activate for 16 hr at 160°C. Deactivate by adding 1% water by weight and mixing for at least 4 hr on a tumbler. Store at room temperature in glass jars fitted with TFE lined screw caps.

6.1.9 Glass wool. Clean glass wool by thorough rinsing with hexane, dried in a 100°C oven, and stored in a hexane rinsed glass jar with TFE lined screw cap.

6.1.10 Boiling chips - silica or carborundum.

6.1.11 GPC Calibration Solutions

6.1.11.1 Corn oil, 200 mg/ml in dichloromethane.

6.1.11.2 Pentachlorophenol and di-n-octylphthalate, 4 mg/ml each in dichloromethane.

6.2 For Identification and Quantitation

6.2.1 Analytical Standards

6.2.1.1 Prepare stock solutions from the pure compounds by dissolving 10 mg quantities into 10 ml of dichloromethane. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.2.1.2 Transfer the stock standard solutions into TFE sealed screw cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, that can be used to determine the accuracy of calibration standards.

6.2.1.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicate a problem.

6.2.1.4 Prepare mixed analytical standards by diluting aliquots of the stock solutions. Analytical standards for all semivolatile compounds should be prepared in three solutions. The acids standard should contain each of the phenolic compounds at concentrations in the range of 50 to 200 ng/μl. Base, neutral, and pesticide (B/N/P) compounds should be split between two solutions, both at concentrations in the range of 20 to 100 ng/μl. One standard should contain the more unstable B/N compounds listed in Table 2, and the second should contain the remaining B/N/P compounds. All working standards must include d_{10}-anthracene at 20 ng/μl.

6.2.1.5 Prepare mixed spiking solutions by serial dilution from the individual stock solutions prepared above. The specifications for spiking solutions for individual samples are described in Section 8.3.2.

7. Method Calibration

7.1 Establish GC/MS operating parameters equivalent to those indicated in Section 12. The GC/MS system can be calibrated using the external standard technique or the internal standard technique.

7.2 External Standard Calibration Procedure

7.2.1 Prepare calibration tandards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with dichloromethane. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 1 to 2 µl of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected in the calibration factor is a constant over the working range (< 10% relative standard deviation RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 Verify the working calibration curve or calibration factor on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.3 Internal Standard Calibration Procedure. To use this approach, select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The internal standards used for this procedure must include d_{10}-anthracene. Because of limitations listed above, no additional internal standards can be suggested that are applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with dichloromethane. One of the standards should be at a concentration near, but above, the method detection limit, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µl of each calibration standard, tabulate peak height or area responses against concentration for each compound and internal standard, and calculate relative response factors (RRF) for each compound using Equation 1.

$$\mathrm{RRF} = (A_s B_{is})/(A_{is} B_s) \qquad \text{(Eq. 1)}$$

where A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

B_{is} = Mass of the internal standard (ng).

B_s = Mass of the parameter to be measured (ng).

If the RRF value over the working range is a constant (< 10% RSD), the RRF can be assumed to be nonvariant and the average RRF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} vs. RRF.

7.3.3 Verify the working calibration curve or RRF on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 Daily Calibration of the GC/MS System

7.4.1 At the beginning of each day, check the calibration of the GC/MS system and adjust if necessary to meet DFTPP specifications (Section 7.4.3). Each day base/neutrals are measured, the column performance specification (Section 12) with benzidine must be met. Each day the acids are measured, the column performance specification (Section 12) with pentachlorophenol must be met. DFTPP can be mixed in solution with either of these compounds to complete two specifications with one injection, if desired.

7.4.2 To perform the calibration test of the GC/MS system, the following instrumental parameters are required.

Electron energy, 70 eV (nominal)

Mass range, m/e 40-475

Scan time, 3 sec or less for acids or base/neutrals with the packed column, 1 sec or less for base/neutrals with the capillary column.

7.4.3 Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP. Inject a solution containing 50 ng DFTPP and check to ensure that performance criteria listed in Table 3 are met. If the system performance criteria are not met, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

7.4.4 At the beginning of each working day, verify the calibration of the GC/MS system by injecting a standard mixture (Section 7.3.3).

7.4.5 For instrument performance verification, to each acid and base/neutral extract and each standard analyzed, add an amount of d_{10}-anthracene immediately prior to injection such that 40 ± 4 ng will be injected.

8. Quality Control

8.1 Demonstrate Acceptable Performance

Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure.

8.1.1 For each compound to be measured, select a spike concentration representative of the expected levels in the samples. Using stock standards, prepare a quality control check standard in acetone 1,000 times more concentrated than the selected concentrations.

8.1.2 Add 80 µl of the check standard to each of a minimum of four 80 ml aliquots of reagent water with a syringe. A representative sludge can be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.1.3 Calculate average recovery (R) and standard deviation (s), in percentage recovery, for the results. Sludge background corrections must be made before R and s calculations are performed.

8.1.4 Using the appropriate data from Tables 13-15, determine the recovery and single operator precision expected for the method for each parameter, and compare these results to the values calculated in Section 8.1.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.1.5 After January 1, 1982, the values for R and s must be rigid method performance criteria provided by the U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, before any samples may be analyzed.

8.2 Precision and Accuracy Statement. The analyst must calculate method performance criteria for each of the surrogate standards.

8.2.1 Calculate upper and lower control limits for method performane for each surrogate standard, using the values for R and s calculated in Section 8.1.3:

Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s

The UCL and LCL can be used to construct control charts[4] that are useful in observing trends in performance. After January 1, 1982, the control limits above must be replaced by method performance criteria provided by the U.S. Environmental Protection Agency.

8.2.2 For each surrogate standard, the laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of sludge as described in Section 8.1.2, followed by the calculation of R and s. Alternately, the analyst must use four sludge data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[6]

8.3 Surrogate Spikes. The laboratory is required to spike all of their samples with the surrogate standard spiking solution to monitor spike recoveries. Suggested surrogate compounds are listed in Table 5. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as described in Section 14.3. The laboratory should monitor the frequency of suspect data to ensure that it remains at or below 5%.

8.4 Method Blank. Before processing any samples, the analyst should demonstrate through the analysis of an 80 ml aliquot of reagent water, that all glassware and reagents are interference free. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.5 Replicate and Spiked Samples

8.5.1 Analyze all samples in duplicate. Using the procedures described in Section 8.3-2, spike and analyze two additional aliquots. Analyze a third unspiked aliquot on the same day that the spiked aliquots are analyzed.

8.5.2 Spike an 80 ml aliquot of sludge with all of the compounds identified in the sample and the representative semivolatile compounds listed in Table 4 at two times the observed concentration or at 10 times the lower limit of detection, whichever is greater. Prepare the spike as two acetone solutions with the acidic and neutral compounds in the first solution and the basic compounds in the second solution. The concentrations of the spiking solutions should be such that 1 to 5 ml of each solution are added to the sludge sample to attain the required spike concentration. Homogenize the spiked sample for 45 to 60 sec and store overnight at 4°C with tumbling before extraction and analysis.

9. Sampling and Preservation

9.1 Sampling. Collect samples in glass containers (1,000 to 4,000 ml) with a TFE lined screw cap. The container should be prewashed with acetone and dried before use. Containers should be filled no more than two-thirds full with sample to minimize breakage during freezing.

9.2 Preservation. Preferably, samples should be iced or refrigerated at 4°C for not more than 24 hr before extraction. Where extraction cannot be performed within 24 hr, samples should be frozen. Samples may be stored for up to 30 days at -20°C or indefinitely at -75°C. In order to prevent breakage during storage, the containers should not be slightly warmed and then recooled. The iced or defrosted sample should be homogenized by mixing for 1 min with a Tissumizer® before analysis.

10. Sample Extraction

10.1 Preparation of Drying Column. Immediately prior to extracting a sample, prepare a drying tube for the extract. Place a small glass wool plug in the bottom of the column and add anhydrous sodium sulfate to a depth of 10 to 15 cm.

10.2 pH Adjustment. Thoroughly mix the sludge sample by homogenizing in the sample bottle for 1 min, then quickly remove a 80 ml aliquot into a 250 ml graduated cylinder. Transfer the aliquot into a 250 ml centrifuge bottle. Basify to pH ≧ 11 with a 6 N sodium hydroxide solution. Mix briefly with the homogenizer to ensure uniform sample pH. (Note: If copious precipitation of carbonates is observed when sodium hydroxide is added, make the sample slightly acidic with 6 N hydrochloric acid and allow the carbon dioxide evolution to cease before basifying the sample.)

10.3 Basic Extraction. Add 80 ml of dichloromethane to the centrifuge bottle and homogenize for 45 to 60 sec. Do not homogenize more than 60 sec to avoid heating the sample. Cap the centrifuge bottles with TFE-lined screw caps and centrifuge at 2,500 to 3,000 rpm for 30 min. Stir and repeat centrifugation if satisfactory phase separation is not achieved. The mixture will separate into an aqueous layer over the dichloromethane extract with a solids cake at the water-dichloromethane interface. Withdraw the extract from each centrifuge bottle with a 100 ml syringe. Discharge the extracts into a 500 ml separatory funnel. Drain the dichloromethane through the drying column into a Kuderna-Danish evaporator. Retain any aqueous layer and return it to the centrifuge bottle. Extract the sample two more times to achieve three-fold extraction. Wash the drying column with an additional 100 ml of dichloromethane and combine the eluent with the dried extracts.

10.4 Extract Concentration. Add a boiling chip to the extract in the Kuderna-Danish evaporator and concentrate the extract to 8 ml using an 85°C bath or a steam bath. If the extract is only slightly colored and not notably viscous, fit a modified Snyder column onto the Kuderna-Danish receiving tube and immerse the tube halfway in a 35°C water bath. Direct a gentle stream of nitrogen directly on the surface of the extract until the volume is ≧ 4 ml. Transfer the extract to a clean vial, seal it with TFE lined screw cap, and store the extract at 4°C. If the extract is highly colored, viscous or solidifies when concentrating to 4 ml, dilute the extract to 12 ml with dichloromethane, transfer to a clean vial, and store as described above.

10.5 Acidic Extraction. Acidifiy the sludge sample portions to pH ≦ 2 with 6 N hydrochloric acid and extract the sample again by procedures described in Sections 10.3 to 10.4. Discard the extracted sludge aliquots.

11. Extract Cleanup

11.1 Base/Neutral Extracts. Clean the base/neutral sludge extracts by adsorption chromatography on either florisil or silica gel. Although there does not appear to be any significant difference in the performance of these adsorbents, the adsorbent selected for analyses of all quality assurance blanks, spiked blanks, and spiked sludges associated with a specific sludge sample must be the same as was selected for the original sample analysis. In cases where the base/neutral extracts are to be analyzed by packed column GC/MS, the GPC procedure (Section 11.2) may be used as an alternative cleanup method.

11.1.1 Column Preparation. Prepare a 200 mm x 20 mm ID silica gel or florisil column by pouring 20 g fresh 3% deactivated silica gel or 1% deactivated florisil, no more than 5 days old, into a chromatographic column containing 60 to 70 ml hexane. Tap the side of the clamped column with a stirring rod to aid packing and air bubble escape. If clumping should occur at the bottom of the solvent reservoir, a stirring rod can be used to break the clumps. Add hexane as needed. After most packing has settled, rinse down the florisil or silica gel adhering to the column walls with additional hexane. Wash the column with an additional 20 ml hexane until the solvent level is within 1 to 2 mm of the top of the silica gel or florisil.

11.1.2 Column Calibration. Check the elution pattern for each new batch of adsorbent prepared by chromatographing a spiked blank. Mix 1 ml of a dichloromethane solution containing 100 μg of each of the specific analytes of interest and the representative B/N/P compounds included in quality assurance method spikes (described in Section 8.3) with 2 g of adsorbant. Evaporate the solvent with a gentle stream of dry nitrogen and add the adsorbant to the column. Elute the column with 20 ml of hexane (Fraction I), 50 ml of 10% dichloromethane in hexane (Fraction II), 50 ml of 50% dichloromethane in hexane (Fraction III), and then 150 ml of 5% acetone in dichloromethane (Fraction V). Maintain the elution flow at 2 to 4 ml/min. Collect each fraction in separate Kuderna-Danish evaporators and concentrate the fractions according to the procedures described in Section 7.4. Analyze each fraction by GC/FID or GC/MS with the SE-54 capillary or packed SP-2250 column. Determine the recovery of each compound in each fraction by comparing the detector responses with those from a duplicate aliquot of the original spiked blank. Elution patterns and recoveries observed for selected compounds chromatographed on silica gel and florisil are shown in Tables 6 and 7. Increasing the volume of Fraction I may be required to provide acceptable cleanup for sludge extracts containing high concentrations of aliphatic hydrocarbons or other non-polar compounds. However, additional hexane may elute significant portions of the chlorinated benzenes, hexachloroethane, hexachlorobutadiene, hexachlorocyclopentadiene, 2-chloronaphthalene, aldrin, and p,p'-DDE. The elution patterns and recoveries observed for many B/N/P compounds chromatographed on silica gel using 100 ml of hexane for Fraction I are shown in Table 8. In cases where the volume of Fraction I must be increased to achieve acceptable cleanup and the analytes of interest include the compounds listed in this section, Fraction I must be analyzed separately from Fraction II-IV.

11.1.3 Column Operation. Place 2 g of fresh 1% deactivated florisil or 3% deactivated silica gel into a small beaker and add the concentrated base/neutral extract. Dry the sample with a gentle nitrogen stream with stirring to ensure fast and uniform drying. Load dried florisil or silica gel containing the sludge components into the column. Elute the column as described in Section 11.1.2. Discard Fraction I. Collect and composite in Kuderna-Danish evaporators all fractions containing the compounds of interest such as Fractions II through IV for all B/N/P compounds. Fraction II frequently contains much higher levels of interfering materials than to Fractions III or IV. As a result, it should not be composited with Fractions III and IV if it contains no compounds of interest. Fractions may be analyzed separately if desired. Concentrate all fractions collected to 1 ml according to procedures described in Section 10.4.

11.2 Acidic Fraction. Use gel permeation chromatography is used to remove triglycerides and fatty acids.

11.2.1 GPC Column Preparation. Place 70 g of Bio-Beads SX-3 in a 400 ml beaker. Cover the beads with dichloromethane and allow the beads to swell overnight before packing the columns. Transfer the swelled beads to the column and start pumping solvent in this case, dichloromethane, through the column, with upward flow at 5.0 ml/min. After ∿ 1 hr, adjust the pressure on the column to 350 to 700 millibars (5 to 10 psi) and pump an additional 4 hr to remove air from the column. Adjust the column pressure periodically as required to maintain 350 to 700 millibars.

11.2.2 Column Calibration. Calibrate the GPC column elution at least once a week according to the following procedure. Load 5 ml of the corn oil solution into sample loop No. 1 and 5 ml of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10 ml fractions, for 36 min, changing the fraction at 2 min intervals. Inject the phenols solution and collect 10-ml fractions for 1 hr. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the SP-2250 and SP-1240-DA columns. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows ≧ 85% removal of the corn oil and ≧ 85% recovery of the di-n-octylphthalate. Choose the "collect time" to extend at least 10 min after the elution of pentachlorophenol. "Wash" the column 20 min between samples. Typical parameters selected are: dump time, 20 min (100 ml); collect time, 30 min (150 ml); and wash time, 20 min (100 ml). The column can also be calibrated using a 254-nm UV detector to monitor the elution of the corn oil and the phenols. Measure the peak areas at various elution times to determine appropriate fractions.

11.2.3 Column Operation. Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage. Load the ≦ 4-ml extracts into the 5-ml loops with a clean solvent on both sides of the extract. Load the ∿ 12-ml extracts in three consecutive loops. Use sufficient clean solvent after the extract to transfer the entire aliquot into the loop. Between extracts, purge the sample loading tubing thoroughly with clean solvent. After especially dirty extracts, run a GPC blank using dichloromethane to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration and collect the cleaned extracts in 250 ml brown bottles. Concentrate the cleaned extracts, combining collected fractions from multiple injections, to ∿ 8 ml using Kuderna-Danish evaporators and then to ≦ 4 ml using modified Snyder columns and nitrogen blowdown. Transfer the cleaned extracts to 8 ml graduated tubes and dilute to 4 ml with dichloromethane. Store at 4°C for GC/MS analysis. Intensely colored extracts may require a second GPC cleanup.

Note: Sample extracts must be in the same solvent used for column elution. Injection of solutions in other solvents can cause a significant change in the bead swell. In extreme cases a traumatic pressure increase may damage the column and cap, or even break the glass column.

12. Sample Extract Analysis

12.1 Base/Neutral/Pesticide Extracts. Analyze the B/N/P extracts by GC/MS using the capillary column or packed column systems described in Section 5.2.1 under the conditions shown below. The capillary column GC/MS procedure is preferred because this procedure provides more unambiguous interpretation of the resulting data. However, if satisfactory performance of the column cannot be demonstrated or if the required Grob-type injection system with direct capillary GC/MS interface is not available, the packed column GC/MS procedure may be used.

12.1.1 Capillary GC/MS with a SE-54 WCOT Column

12.1.1.1 Column Temperature: 50°C for 4 min, 50 to 320°C at 4°C/min, and 320°C until after the elution time for benzo[*g*,*h*,*i*]perylene.

GC/MS interface, 300°C

Carrier gas helium at 10 psi

Splitless injection for 30 sec

Injection size, 2 µl

Examples of the separations achieved by this column are shown in Figure 2. Relative retention times for the base/neutral compounds on this column are listed in Table 9.

12.1.1.2 Capillary Column GC/MS Performance Checks

12.1.1.2.a Column Performance Screening. Fully evaluate the performance of each new column by GC/FID prior to installation in the GC/MS system.[5] In addition, recheck columns that show a marked decrease in performance on the GC/MS (as described in Section 12.2.1.3) or that have not been used the previous 2 weeks for GC/MS analyses under this protocol. Install the capillary column in a gas chromatograph equipped with a Grob-type split/splitless injector and flame ionization detector. Adjust carrier gas at about 15 to 20 cm/sec for N_2 or 30 to 40 cm/sec when He or hydrogen are used as the carrier gas. Set the splitter flow at 30 to 50 ml/min, makeup gas at 30 ml/min, and column oven temperature at 85°C. Using splitless injection, inject 2 μl of a column performance test mixture containing 20 ng each of 2,6-dimethylphenol, 2,6-dimethylaniline, 1-octanol, 2-octanone, _n_-tridecane, and n-tetradecane or an equivalent commercial test mixture. Table 10 shows the contents of three appropriate commercial mixtures. Measure the pH of the column as the ratio of the peak height of 2,6-dimethylaniline to that of 2,6-dimethylphenol. A value of 0.5 to 1.5 is acceptable. Determine the activity of the column toward polar compounds by determining both the asymmetry for the 1-octanol peak and the ratio of the peak height of 1-octanol to that of C_{13} alkane. The peak asymmetry is evaluated by drawing a perpendicular from the apex of the peak to the baseline and measuring the width from the front of the peak to the perpendicular line (W_F) and from the back of the peak to the perpendicular line (W_B).

$$AS = \frac{W_B}{W_F} \times 100$$

Peak asymmetries between 75 and 200 are acceptable. The ratio of peak height of the 1-octanol to that of C_{13} alkane should be higher than 0.5. Determine the number of effective theoretical plates (N_{eff}) from the tridecane peak using the equation

$$N_{eff} = 5.545 \left(\frac{tr'}{W_{0.5}}\right)^2$$

where tr' is the adjusted retention time of tridecane and $W_{0.5}$ is the peak width at half height. The number of effective plates of acceptable columns must be at least 25,000.

12.1.1.2.b System Performance. Evaluate the performance of the capillary column in the GC/MS system each time the column is installed and each working day prior to its use. Using splitless injection, inject 2 μl of a test mixture containing 20 ng each of 2,6-dimethylaniline, 2,6-dimethylphenol, DFTPP, methylstearate, octadecene, and octadecane. Measure the pH of the column by taking the ratio of peak heights of 2,6-dimethylaniline to that of 2,6-dimethylphenol. A pH of 0.5 to 1.5 is acceptable. Determine the resolution of the peaks corresponding to octadecane and octadecane. The peaks should be resolved with no more than a 50% valley. Determine the asymmetry of the methylstearate peak according to the formula given in Section 12.1.1.2.a. If the methylstearate peak tails, the GC/MS transfer line is not adequately heated.

12.1.1.3 At the beginning of each day that base/neutral analyses are to be performed, inject 100 ng of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. Acceptable performance is achieved when the benzidine is identified according to Section 13.

12.1.2 Packed Column GC/MS with a SP-2250 Column

12.1.2.1 Chromatographic Conditions

Column temperature, 60°C for 2 min, 60 to 260°C at 80°C/min, and 260°C until after the elution time for benz[g,h,i]perylene.

Injector temperature, 225°C

GC/MS interface temperature, 275°C

Carrier gas, helium at 30 ml/min

Injection size, 2 μl

An example of the separation achieved by the column is shown in Figure 3. Relative retention times for the base/neutral and pesticide compounds on this column are listed in Table 11.

12.1.2.2 At the beginning of each day that base/neutral analyses are to be performed, inject 100 ng of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. Acceptable performance is achieved when the benzidine is identified according to Section 13.

12.2 Acid Extracts

12.2.1 Analyze acid extracts by GC/MS using the SP-1240-DA column described in Section 5.2.1, operated under the following conditions.

Column temperature, 85°C for 2 min, 85 to 185°C at 10°C/min and 185°C until after the elution time for 4-nitrophenol.

Injector temperature, 185°C.

GC/MS surface temperature, 275°C.

Carrier gas, helium at 30 ml/min.

Injection size, 2 µl.

An example of the separation achieved by the column is shown in Figure 4. Relative retention times for the acid compounds are listed in Table 11.

12.2.2 At the beginning of each day that acid fraction analyses are to be performed, inject 50 ng of pentachlorophenol either separately or as part of a standard mixture that may also contain DFTPP. Acceptable performance is achieved when pentachlorophenol is identified according to Section 13.

13. Qualitative and Quantitative Determination

13.1 Using the characteristic mass spectral ions listed in Tables 8 or 10 for the base/neutral and pesticide compounds and in Table 11 for the acid compounds, plot at least three extracted ion current plots (EICPs) for each analyte.

13.2 Identify the presence of analytes by the coincidence of peaks in the characteristic EICPs at the appropriate retention times and with intensities in the characteristic ratios (Tables 8 or 10 and 11).

13.3 Record the area (intensity) of the peak in the EICP for the most intense ion for each compound identified.

14. Calculations

14.1 Determine the concentration of individual compounds in the sample.

14.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated from Equation 2:

$$\text{Concentration, } \mu\text{g/liter} = \frac{(M)(V_E)}{(V_I)(V_s)} \qquad \text{(Eq. 2)}$$

where: M = Mass of material injected (ng).

V_I = Volume of extract injected (µl).

V_E = Volume of total extract (ml).

V_s = Volume of wet sludge extracted (liter)

14.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using Equation 3.

$$\text{Concentration, } \mu g/\text{liter} = \frac{(A)(I_s)(V_E)}{(A_{IS})(RRF)(V_I)(V_s)} \qquad \text{(Eq. 3)}$$

where: A = Area of peak in sample extract.

A_{IS} = Area of internal standard peak in sample extract.

I_S = Areas of internal standard injected (ng).

V_E = Total volume of extract (ml).

V_I = Volume of extract injected (µl).

V_s = Volume of sludge extracted (liter).

RRF = Relative response factor.

14.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

14.3 If the surrogate standard recoverues fall outside the limits in Section 8.2, data for all parameters in that sample must be labeled as suspect.

15. Method Performance

Performance data for the application of this method to both POTW and industrial sludges are shown in Tables 13 to 15. Table 13 shows data for B/N compounds analyzed in POTW and industrial sludges via Option A. Table 14 shows data for B/N compounds analyzed via Option B and acidic compounds in aliquots of the same sludges. Data for B/N compound were analyzed via Option B and acidic compounds in sludges from 40 POTWs. Most of these data represent results from one laboratory. Approximately 25% of the data in Table 15 was contributed by a second laboratory.

16. References

1. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2. "OSHA Safety and Health Standards, General Industry" (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised January 1979).

3. "Safety in Academic Chemistry Laboratories," American Chemical Society Committee on Chemical Safety, 3rd Edition Publication (1979).

4. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

5. Grob, K., Jr., G. Grob, and K. Grob, "Comprehensive Standardized Quality Test for Glass Capillary Columns," J. Chrom., 156, 1-20 (1978).

17. Additional Sources

1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants." U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, March 1977, Revised April 1977. Effluent Guidelines Division, Washington, DC 20460.

2. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, OH 45268. In preparation.

3. "Preservation and Maximum Holding Time for the Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268. In preparation.

4. Budde, W. L., and J. W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, p. 16, April 1980.

5. Kleopfer, R. D., "Priority Pollutant Methodology Quality Assurance Review," U.S. Environmental Protection Agency, Region VII, Kansas City, KS. Seminar for Analytical Methods for Priority Pollutants, Norfolk, VA, January 17-18, 1980, U.S. Environmental Protection Agency, Office of Water Programs, Effluent Guidelines Division, Washington, DC 20460.

TABLE 1. EXTRACTABLE ORGANIC PRIORITY POLLUTANTS

Compound	STORET No.	CAS No.
Acids		
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	32730	108-95-2
2,4,5-Trichlorophenol	34621	88-06-2
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
4,6-Dinitro-2-methylphenol	34657	534-32-1
Bases		
Benzidine	39210	93-87-5
3,3'-Dichlorobenzidine	34631	92-94-1
Polycyclic Aromatic Hydrocarbons		
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34461	120-12-7
Benz[*a*]anthracene	34562	56-55-3
Benzo[*b*]fluoranthene	34242	205-99-2
Benzo[*k*]fluoranthene	34242	207-08-9
Benzo[*g*,*h*,*i*]perylene	34521	191-24-2
Benzo[*a*]pyrene	34247	50-32-8
Chrysene	34562	218-01-9
Dibenz[*a*,*h*]anthracene	34556	53-70-3
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Indeno[1,2,3-*cd*]pyrene	34403	193-39-5
Naphthalene	39250	91-20-3
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
Phthalates		
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Butylbenzylphthalate	34292	85-68-7
Diethylphthalate	34336	84-66-2
Dimethylphthalate	34341	131-11-3
Di-*n*-butylphthalate	39110	84-74-2
Di-*n*-octylphthalate	34596	117-84-0

(continued)

TABLE 1 (continued)

Compound	STORET No.	CAS No.
Chlorinated Hydrocarbons		
2-Chloronaphthalene	34581	91-58-7
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
Hexachlorobenzene	39700	118-74-1
Hexachloro-1,3-butadiene	34391	87-68-3
Hexachloroethane	34396	67-72-1
Hexachlorocyclopentadiene	34386	77-47-4
1,2,4-Trichlorobenzene	34551	129-82-1
Chloroalkyl Ethers		
Bis(2-chloroethyl)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-chloroisopropyl)ether	34283	39638-32-9
Miscellaneous Neutrals		
4-Bromophenyl phenyl ether	34636	101-55-3
4-Chlorophenyl phenyl ether	34641	7005-72-3
2,4-Dinitrotoluene	34611	121-14-2
N-Nitrosodi-*n*-propylamine	34428	621-64-7
N-Nitrosodimethylamine	34438	62-75-9
2,6-Dinitrotoluene	34626	606-20-2
Isophorone	34408	78-59-1
Nitrobenzene	34447	98-95-3
N-Nitrosodiphenylamine	34433	86-30-6
1,2-Diphenylhydrazine	34346	122-66-7
Pesticides		
β-Endosulfan	34356	33213-65-9
α-BHC	39337	319-84-6
γ-BHC	34264	58-89-9
β-BHC	39338	319-85-7
Aldrin	39330	309-00-2
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
α-Endosulfan	34361	959-98-8
Dieldrin	39380	60-57-1
4,4'-DDE	39320	72-55-9
4,4'-DDD	39310	72-54-8
4,4'-DDT	39300	50-29-3

(continued)

TABLE 1 (concluded)

Compound	STORET No.	CAS No.
Endrin	39390	72-20-8
Endosulfan sulfate	34351	1031-07-8
δ-BHC	34259	319-86-8
Chlordane	39350	57-74-9
Toxaphene	39400	8001-35-2
PCB-1242	39496	53469-21-9
PCB-1221	39504	11104-28-2
PCB-1254	39488	11097-69-1
PCB-1232	39492	11141-16-5
PCB-1248	39500	12672-29-6
PCB-1260	39508	11096-82-5
PCB-1016	34671	12674-11-2

TABLE 2. UNSTABLE B/N COMPOUNDS

Bis(2-chloroisopropyl)ether
Nitrobenzene
N-Nitroso-di-n-propylamine
Bis(2-chloroethoxy)methane
Isophorone
2,6-Dinitrotoluene
2,4-Dinitrotoluene
1,2-Diphenylhydrazine
Benzidine
3,3'-Dichlorobenzidine
N-Nitrosodimethylamine

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

m/e	Ion abundance criteria
51	30-60% of m/e 198
68	< 2% of m/e 69
70	< 2% of m/e 69
127	40-60% of 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of m/e 198
275	10-30% of m/e 198
365	1% of m/e 198
441	Present and < m/e 443
442	40% of m/e 198
443	17-23% of m/e 442

[a] Eichelberger, J. W., L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995 (1975).

TABLE 4. REPRESENTATIVE EXTRACTABLE COMPOUNDS FOR RECOVERY STUDIES

Acenaphthylene
Benzidine
Benzo[a]pyrene
Bis(2-chloroethyl) ether
Bis(2-chloroisopropyl) ether
Bis(2-ethylhexyl)phthalate
Butylbenzyl phthalate
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,4-Dimethylphenol
2,6-Dinitrotoluene
Fluoranthene
Hexachloroethane
N-Nitrosodimethylamine
1,4-Dichlorobenzene
Pentachlorophenol
Phenol
Dieldrin
α-BHC
p,p'-DDE
Heptachlor

TABLE 5. SUGGESTED SURROGATE STANDARDS

Base/neutral fraction	Acid fraction
Aniline-d_5	2-Fluorophenol
Anthracene-d_{10}	Pentafluorophenol
Benzo[a]anthracene-d_{12}	Phenol-d_5
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
2-Fluoraniline	
1-Fluoronaphthylene	
2-Fluoronaphthylene	
Naphthalene-d_8	
Nitrobenzene-d_5	
1,2,3,4,5-Pentafluorobiphenyl	
Phenanthrene-d_{10}	
Pyridine-d_5	

TABLE 6. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRALS CHROMATOGRAPHED ON SILICA GEL[a]

Compound	Spike level (µg)	Fraction I hexane (20 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[b] (%)
1,4-Dichlorobenzene	46.8		+[c]	+		70
Hexachloroethane	31.2		+			83
Bis(2-chloroisopropyl)ether)	49.6				+	85
Bis(2-chloroethyl)ether	31.6				+	93
Acenaphthylene	28.5			+		79
2,6-Dinitrotoluene	35.1				+	96
Fluoranthene	27.0			+		90
Benzidine	31.0					0
3,3'-Dichlorobenzidine	36.4				+	50
n-Butylbenzylphthalate	45.2				+	97
Bis(2-ethylhexyl)phthalate	39.6				+	93
Benzo[a]pyrene	30.0			+		78

a 3% deactivated silica gel.

b Analyses done by packed column GC/MS.

c + indicates more than 1% recovery in that fraction.

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TABLE 7. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRALS CHROMATOGRAPHED ON FLORISIL[a]

Compound	Spike level (μg)	Fraction I hexane (20 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[b] (%)
1,4-Dichlorobenzene	93.6		+[c]	+	+	48
Hexachloroethane	62.4		+	+	+	67
Bis(2-chloroisopropyl)ether	42.2			+	+	152
Bis(2-chloroethyl)ether	66.2			+	+	48
Acenaphthylene	57.0		+	+	+	92
2,6-Dinitrotoluene	70.2				+	125
Fluoranthene	54.0		+	+	+	121
Benzidine	62.0					0
3,3'-Dichlorobenzidine	72.8				+	65
n-Butylbenzylphthalate	90.4				+	106
Bis(2-ethylhexyl)phthalate	79.2				+	92
Benzo[a]pyrene	60.0			+	+	87

[a] 1% deactivated florisil.

[b] Analyses done by packed column GC/MS.

[c] + indicates more than 1% recovery in that fraction.

TABLE 8. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRAL/PESTICIDES CHROMATOGRAPHED ON SILICA GEL WITH AN ALTERNATE ELUTION[a,b] SCHEME

Compound	Fraction I hexane (100 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[c] (%)
Bis(2-chloroethyl)ether				+[d]	95 ± 22
1,3-Dichlorobenzene	+				64 ± 6
1,2-Dichlorobenzene	+				67 ± 9
Hexachloroethane	+				73 ± 14
N-nitrosodi-n-propylamine				+	94 ± 12
Nitrobenzene			+	+	67 ± 3
Bis(2-chloroethoxy)methane				+	66 ± 5
1,2,4-Trichlorobenzene	+				70 ± 17
Naphthalene	+	+	+		58 ± 7
Hexachlorobutadiene	+				142 ± 51
Hexachlorocyclopentadiene	+				300 ± 55
2-Chloronaphthalene	+	+			94 ± 5
Acenaphthylene		+	+		77 ± 21
2,6-Dinitrotoluene				+	93 ± 19
Acenaphthalene		+	+		88 ± 12
2,4-Dinitrotoluene				+	95 ± 14
Fluorene			+		87 ± 22
4-Chlorophenylphenylether			+		109 ± 12
Diethylphthalate				+	90 ± 41
4-Bromophenylphenylether			+		116 ± 15
Hexachlorobenzene	+				85 ± 30
Phenanthrene			+		85 ± 30
Anthracene			+		83 ± 28

(continued)

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TABLE 8 (continued)

Compound	Fraction I hexane (100 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[c] (%)
Di-n-butylphthalate				+	80 ± 51
Fluoranthene			+		51 ± 20
Pyrene			+		63 ± 12
Endosulfan sulfate				+	67 ± 17
n-Butylbenzylphthalate				+	87 ± 35
Chrysene			+		72 ± 5
3,3'-Dichlorobenzidine				+	40 ± 2
Bis(2-ethylhexyl)phthalate				+	95 ± 61
Benzo[a]pyrene			+		70 ± 34
Dibenz[a,h]anthracene			+		84 ± 17
γ-BHC		+	+	+	66 ± 27
Aldrin	+				67 ± 14
Heptachlorepoxide			+	+	88 ± 3
p,p'-DDE	+	+	+		80 ± 6
Endrin				+	77 ± 18
p,p'-DDD			+		78 ± 7
p,p'-DDT			+	+	91 ± 17
α-Endosulfan			+	+	86 ± 17

[a] Data from Lopez-Avila, Viorica, Raymond V. Northcutt, Jon Onstot, and Margie Wickham. "Analysis of the NBS Sediment by the MRI Sludge Protocol," Final Report prepared for the Environmental Protection Agency under EPA Contract No. 68-03-2711 (1981).

[b] 1% reactivated silica gel.

[c] Recoveries determined in duplicate at 8-μg and 80-μg levels for each compound. Analyses done by fused silica capillary GC/MS.

[d] + indicates more than 1% recovery in that fraction.

TABLE 9. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC EI IONS FOR THE BASE/NEUTRAL COMPOUND ANALYZED BY CAPILLARY COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
N-Nitrosodimethylamine	0.04	42(100), 74(88), 44(21)
Bis(2-chloroethyl)ether	0.21	93(100), 63(99), 95(31)
1,3-Dichlorobenzene	0.22	146(100), 148(64), 113(12)
1,4-Dichlorobenzene	0.22	146(100), 148(64), 113(11)
1,2-Dichlorobenzene	0.25	146(100), 148(64), 113 (11)
Bis(2-chloroisopropyl)ether	0.29	45(100), 77(19), 79(12)
Hexachloroethane	0.29	117(100, 199(61), 201(99)
N-Nitrosodi-n-propylamine	0.31	130(22), 42(64), 101(12)
Nitrobenzene	0.32	77(100), 123(50), 65(15)
Isophorone	0.36	82(100), 95(14), 138(18)
Bis(2-chloroethoxy)methane	0.41	93(100), 95(32), 123(21)
1,2,4-Trichlorobenzene	0.42	74(100), 109(80), 145(52)
Naphthalene	0.43	128(100), 223(63), 227(65)
Hexachlorobutadiene	0.47	225(100), 223(63), 227(65)
Hexachlorocyclopentadiene	0.60	237(100), 235(63), 272(12)
2-Chloronaphthalene	0.63	162(100), 164(32), 127(31)
Acenaphthylene	0.70	152(100), 153(16), 151(17)
Dimethylphthalate	0.72	163(100), 164(10), 194(11)
2,6-Dinitrotoluene	0.72	165(100), 63(72), 121(23)
Acenaphthene	0.73	154(100), 155(95), 152(13)
2,4-Dinitrotoluene	0.78	165(100), 63(72), 121(23)
Fluorene	0.82	166(100), 165(80), 167(14)
4-Chlorophenyl phenyl ether	0.84	204(100), 206(34), 141(29)
Diethylphthalate	0.84	149(100), 178(25), 150(10)
N-Nitrosodiphenylamine[c]	0.84	169(100), 168(71), 167(50)
1,2-Diphenylhydrazine[d]	0.86	77(100), 93(58), 105(28)
4-Bromophenyl phenyl ether	0.92	248(100), 250(99), 141(45)
Hexachlorobenzene	0.93	284(100), 142(30), 249(24)
Phenanthrene	0.98	178(100), 179(16), 176(15)
Anthracene	0.99	178(100), 179(16), 176(15)
d_{10}-Anthracene	1.00	188(100), 94(19), 80(18)
Di-n-butylphthalate	1.14	149(100), 150(27), 104(10)
Fluoranthene	1.19	202(100), 101(23), 100(14)
Pyrene	1.23	202(100), 101(26), 100(17)
Benzidene	1.24	184(100), 92(24), 185(13)
Butylbenzylphthalate	1.40	149(100), 91(50)
Chrysene	1.45	228(100), 229(19), 226(23)
3,3'-Dichlorobenzidene	1.47	252(100), 254(66), 126(16)
Bis(2-ethylhexyl)phthalate	1.52	149(100), 167(31), 279(26)
Benzo[k]fluoranthene	1.62	252(100), 253(23), 125(16)

(continued)

TABLE 9 (continued)

Compound	RRT^{a,b}	Characteristic EI ions (relative intensity)
Di-n-octylphthalate	1.63	149(100), 167(29), 279(22)
Benzo[a]pyrene	1.67	252(100), 253(23), 125(21)
Dibenz[a,h]anthracene	1.84	278(100), 139(31), 279(12)
Benzo[g,h,i]perylene	1.87	276(100), 138(37), 277(25)

a Relative to d_{10}-anthracene. Retention times data were not determined for the priority pollutant pesticides and a few base/neutral compounds. However, their retention properties should be roughly equivalent to those on SP-2250 (see Table 6).

b SE-54 WCOT glass capillary (15 m x 0.24 mm ID), He at 10 psi, program: 50°C for 4 min, then 4°C/min to 320°C.

c Elutes as diphenylamine.

d Elutes as azobenzene.

TABLE 10. COMPOSITION OF CAPILLARY COLUMN PERFORMANCE TEST MIXTURES

Test mixture	Composition	
Varian P/N 82-005049-01 (nonpolar)	2-octanone	0.2 μg/μl
	1-octanol	0.2
	naphthalene	0.2
	2,6-dimethylphenol	0.2
	2,4-dimethylaniline	0.2
	C_{12}-alkane	0.2
	C_{13}-alkane	0.2
Alltech TP-5 (polar)	C_{13}-alkane	0.1 μg/μl
	C_{14}-alkane	0.1
	C_{15}-alkane	0.1
	C_{16}-alkane	0.1
	1-octanol	0.5
	5-nonanone	0.3
	2,6-dimethylaniline	0.4
	2,6-dimethylphenol	0.4
	naphthalene	0.5
Analabs Test probe LPK-013F (general purpose)	C_{12}-acid methyl ester	41 ng/μl
	C_{11}-acid methyl ester	41
	C_{10}-acid methyl ester	42
	C_{10}-alkane	28
	C_{11}-alkane	29
	1-octanol	36
	Nonanal	40
	2,3-butanediol	53
	2,6-dimethylphenol	32
	2,6-dimethylaniline	32
	dicyclohexylamine	31
	2-ethylhexanoic acid	38

TABLE 11. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC IONS FOR THE BASE/NEUTRAL AND PESTICIDE COMPOUNDS ANALYZED BY PACKED COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
N-Nitrosodimethylamine	0.15	42(100), 74(88), 44(21)
1,3-Dichlorobenzene	0.31	146(100), 148(64), 113(12)
1,4-Dichlorobenzene	0.33	146(100), 148(64), 113(11)
Hexachloroethane	0.35	117(100), 199(61), 201(99)
1,2-Dichlorobenzene	0.35	146(100), 140(64), 113(11)
Bis(2-chloroisopropyl)ether	0.37	45(100), 77(19), 79(12)
N-Nitrosodi-n-propylamine	0.42	130(22), 42(64), 101(12)
Nitrobenzene	0.45	77(100), 123(50), 65(15)
Isophorone	0.47	82(100), 95(14), 138(18)
Hexachlorobutadiene	0.48	225(100), 223(63), 227(65)
1,2,4-Trichlorobenzene	0.49	74(100), 109(80), 145(52)
Bis(2-chloroethoxy)methane	0.50	93(100), 95(32), 123(21)
Naphthalene	0.51	128(100), 127(10), 129(11)
Bis(2-chloroethyl)ether	0.55	93(100), 63(99), 95(31)
Hexachlorocyclopentadiene	0.60	237(100), 235(63), 272(12)
2-Chloronaphthalene	0.68	162(100), 164(32), 127(31)
Acenaphthylene	0.75	152(100), 153(16), 151(17)
Acenaphthene	0.77	154(100), 153(95), 152(53)
Dimethyl phthalate	0.78	163(100), 164(10), 194(11)
2,6-Dinitrotoluene	0.81	165(100), 63(72), 121(23)
Fluorene	0.85	166(100), 165(80), 167(14)
2,4-Dinitrotoluene	0.85	165(100), 63(72), 121(23)
4-Chlorophenyl phenyl ether	0.85	204(100), 206(34), 141(29)
Diethyl phthalate	0.87	149(100), 178(25), 150(10)
1,2-Diphenylhydrazine[b]	0.88	77(100), 93(58), 105(28)
N-Nitrosodiphenylamine[c]	0.89	169(100), 168(71), 167(50)
Hexachlorobenzene	0.92	284(100), 142(30), 249(24)
4-Bromophenyl phenyl ether	0.92	248(100), 250(99), 141(45)
Phenanthrene	0.99	178(100), 179(16), 176(15)
Anthracene	0.99	178(100), 179(16), 176(15)
Deuterated anthracene (D-10)	1.00	188(100), 94(19), 80(18)
D-n-butylphthalate	1.09	149(100), 150(27), 104(10)
Fluoranthene	1.18	202(100), 101(23), 100(14)
Pyrene	1.22	202(100), 101(26), 100(17)
Benzidine	1.27	184(100), 92(24), 185(13)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1.33	322(100), 320(90), 59(95)
Butylbenzylphthalate	1.34	149(100), 91(50)
Bis(2-ethylhexyl)phthalate	1.37	149(100), 167(31), 279(26)
Chrysene	1.40	228(100), 229(19), 226(23)

(continued)

TABLE 11 (continued)

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
Benz[*a*]anthracene	1.40	228(100), 229(19), 226(19)
Benzo[*b*]fluoranthene	1.43	252(100), 253(23), 125(15)
Benzo[*k*]fluoranthene	1.43	252(100), 253(23), 125(16)
3,3'-Dichlorobenzidine	1.45	252(100), 254(66), 126(16)
Di-n-octylphthalate	1.50	149(100), 167, 279
Benzo[*a*]pyrene	1.50	252(100), 253(23), 125(21)
Indeno[1,2,3-*cd*]pyrene	1.86	276(100), 138(28), 277(27)
Benzo[*g*,*h*,*i*]perylene	1.98	276(100), 138(37), 277(25)
Bis(chloromethyl) ether	d	45(100), 49(14), 51(5)
β-Endosulfan	0.47	201(100), 283(48), 278(30)
α-BHC	0.94	183(100), 109(86), 181(91)
γ-BHC	1.00	183(100), 109(86), 181(91)
β-BHC	1.03	181(100), 183(93), 109(62)
δ-BHC	1.04	183(100), 109(86), 181(90)
Aldrin	1.05	181(100), 183(93), 109(62)
Heptachlor	1.06	183(100), 109(86), 181(90)
Heptachlor epoxide	1.13	66(100), 220(11), 263(73)
α-Endosulfan	1.14	100(100), 353(79), 351(60)
Dieldrin	1.18	201(100), 283(48), 278(30)
4,4'-DDE	1.20	79(100), 263(28), 279(22)
4,4'-DDD	1.22	246(100), 248(64), 176(65)
4,4'-DDT	1.27	235(100), 237(76), 165(93)
Endrin	1.30	81(100), 82(61), 263(70)
Endosulfan sulfate	1.30	272(100), 387(75), 422(25)
Chlordane	1.05-1.26	373(19), 375(17), 377(10)[e]
Toxaphene	1.12-1.35	(231, 233, 235)[f]
PCB-1242	0.86-1.14	(224, 260, 294)[f]
PCB-1254	1.09-1.30	(294, 330, 362)[f]

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[a] 3% SP-2250 on 100/120 mesh Supelcoport in a 1.8 m x 2 mm ID glass column; He at 30 ml/min. Program: 60°C for 2 min, then 8°C/min to 260°C and hold for 15 min.

[b] Elutes as azobenzene.

[c] Elutes as diphenylamine.

[d] No data.

[e] These three ions are characteristic for the α and γ forms of chlordane. No stock should be set in these three for other isomers.

[f] These ions are listed without relative intensities since the mixtures they represent defy characterization by three masses.

TABLE 12. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC IONS FOR THE ACID COMPOUNDS ANALYZED BY PACKED COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
Chlorophenol	0.51	128(100), 64(54), 130(31)
2-Nitrophenol	0.55	139(100), 65(35), 109(8)
Phenol	0.61	94(100), 65(17), 66(19)
2,4-Dimethylphenol	0.67	122(100), 107(90), 121(55)
2,4-Dichlorophenol	0.69	162(100), 164(50), 98(61)
2,4,6-Trichlorophenol	0.79	196(100), 198(92), 200(26)
4-Chloro-m-cresol	0.86	142(100), 107(80), 144(32)
2,4-Dinitrophenol	1.04	184(100), 63(59), 154(53)
4,6-Dinitro-o-cresol	1.04	198(100), 182(35), 77(28)
Pentachlorophenol	1.13	266(100), 264(62), 268(63)
4-Nitrophenol	1.63	65(100), 139(45), 109(72)

[a] Relative to d_{10}-anthracene.

[b] 1% SP-1240-DA on 100/120 Supelcoport in a 1.2 m x 2 mm ID glass column; He at 30 ml/min. Program: 85°C for 2 min, then 10°C/min to 185°C and hold for 5 min.

TABLE 13. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION A (SILICA GEL CLEANUP, HRGC/MS DETERMINATION) IN THREE POTW AND TWO INDUSTRIAL SLUDGES

	Three POTW sludges						Two industrial sludges					
				Spike recovery						Spike recovery		
		Spike level (µg/ℓ)						Spike level (µg/ℓ)				
Compound	Determinations	Minimum	Maximum	Mean (%)	Standard deviation	Mean RSD for Tripl. (%)	Determinations	Minimum	Maximum	Mean (%)	Standard deviation	Mean RSD for Tripl. (%)
1,4-Dichlorobenzene	27	400	40,000	44	25	37	18	400	40,000	65	59	32
Hexachloroethane	25	400	40,000	24	17	33	18	400	40,000	55	65	55
Bis(2-chloroethyl)ether	27	400	40,000	110	77	54	16	400	40,000	80	44	20
Acenaphthylene	27	400	40,000	110	66	26	15	400	40,000	95	27	14
2,6-Dinitrotoluene	25	400	40,000	33	35	72	15	400	40,000	89	63	42
Fluoranthene	24	400	40,000	140	64	25	15	400	40,000	110	42	18
Benzidine	18	7,900	80,000	31	31	49	12	780	80,000	120	96	25
3,3'-Dichlorobenzidine	9	402	4,130	50	78	66	[a]	-	-	-	-	-
Butylbenzylphthalate	18	4,000	40,000	140	59	18	12	400	40,000	130	92	19
Di-n-octylphthalate	18	400	40,000	130	75	40	15	400	48,800	130	71	30
Benzo[a]pyrene	21	400	40,000	110	43	24	15	400	40,100	82	70	30

[a] This compound was not spiked into the industrial sludges.

TABLE 14. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION B (GPC CLEANUP, GC/MS DETERMINATION AND ACIDIC EXTRACTABLE ORGANICS IN THREE POTW AND TWO INDUSTRIAL SLUDGES

	Three POTW sludges						Two industrial sludges					
				Spike recovery						Spike recovery		
		Spike level (µg/ℓ)						Spike level (µg/ℓ)				
Compound	Determinations	Minimum	Maximum	Mean (%)	Standard deviation	Mean RSD for Tripl. (%)	Determinations	Minimum	Maximum	Mean (%)	Standard deviation	Mean RSD for Tripl. (%)
1,4-Dichlorobenzene	27	40	41,600	69	28	16	15	400	40,000	75	16	9
Hexachloroethane	23	400	44,100	48	17	10	16	400	40,000	56	31	14
Bis(2-chloroethyl)ether	25	400	40,700	220	190	17	16	400	40,000	120	51	7
Acenaphthylene	21	400	40,000	65	26	9	18	400	40,000	110	47	12
2,6-Dinitrotoluene	14	4,000	40,000	50	31	10	12	4,000	40,000	100	35	10
Fluoranthene	24	400	40,000	51	27	14	15	400	40,000	91	22	8
Benzidine	14	4,870	80,000	79	59	8	16	800	70,000	77	41	10
3,3'-Dichlorobenzidine	13	415	4,130	69	40	11	3	4,000	4,000	110	13	13
Butylbenzylphthalate	18	4,500	40,000	130	120	7	12	400	40,000	69	15	9
Di-n-octylphthalate	28	4,000	40,000	98	77	13	12	400	48,800	81	73	10
Benzo[a]pyrene	16	400	40,600	120	94	13	16	400	40,000	66	47	7
Phenol	24	400	46,300	73	26	27	14	400	40,000	72	34	26
2,4-Dimethylphenol	26	400	41,100	58	62	37	12	400	40,000	110	64	23
2,4-Dichlorophenol	21	399	40,000	89	32	18	15	400	40,000	140	96	15
Pentachlorophenol	26	400	40,000	120	67	37	10	400	40,000	50	16	28

TABLE 15. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION B (GPC CLEANUP, GC/MS DETERMINATIONS) AND ACIDIC EXTRACTABLE ORGANICS IN PRIMARY SLUDGES FROM 40 POTWs[a]

Compound	Determinations	Spike recovery[b] Mean (%)	Standard Deviation	Mean Avg. Rel. Dev. for Dupl.
1,3-Dichlorobenzene	27	86	39	11
1,2-Dichlorobenzene	24	68	25	11
Nitrobenzene	13	49	28	17
Hexachlorobutadiene	27	71	22	7
Naphthalene	27	94	37	8
2-Chloronaphthalene	27	89	33	8
Acenaphthalene	24	79	27	8
2,6-Dinitrotoluene	23	59	38	15
Fluorene	27	94	34	10
N-Nitrosodiphenylamine	24	140	84	11
4-Bromophenylphenylether	27	80	27	5
Di-n-butylphthalate	26	79	43	9
Fluoranthene	26	85	40	9
Pyrene	27	90	47	8
Butylbenzylphthalate	26	95	64	11
Bis(2-ethylhexyl)phthalate	22	65	34	8
Benzo[a]pyrene	27	85	49	11
1,4-Dichlorobenzene	27	82	34	11
Hexachloroethane	21	49	25	21
Isophorone	27	51	27	15
1,2,4-Trichlorobenzene	27	83	32	9
Bis(2-chloroethoxy)methane	24	54	27	12
Hexachlorocyclopentadiene	20	0	0	0
Acenaphthylene	19	76	24	9
Dimethylphthalate	27	50	33	20
2,4-Dinitrotoluene	26	65	50	14
Diethylphthalate	27	65	35	12
Hexachlorobenzene	27	63	21	10
Phenanthrene/anthracene	26	71	39	11
Chrysene/Benz[a]anthracene	27	71	27	11
Benzo[g,h,i]perylene	19	31	15	10
N-Nitrosodi-N-propylamine	24	77	54	13
1,2-Diphenylhydrazine	23	64	30	9
Benzidine	21	8	11	15
3,3'-Dichlorobenzidine	27	56	58	14
2-Chlorophenol	27	59	16	14
2-Nitrophenol	27	46	39	17
4-Nitrophenol	25	22	23	15
Phenol	26	66	28	11

(continued)

TABLE 15 (continued)

Compound	Determinations	Spike recovery[b]		
		Mean (%)	Standard Deviation	Mean Avg. Rel. Dev. for Dupl.
2,4-Dimethylphenol	27	34	39	20
2,4-Dichlorophenol	27	68	25	11
2,4,6-Trichlorophenol	27	71	25	13
1,3-Dichlorobenzene	27	86	39	11
p-Chloro-*m*-cresol	22	58	32	9
2,4-Dinitrophenol	24	14	27	11
4,6-Dinitro-*o*-cresol	26	13	24	15
Pentachlorophenol	27	84	43	15
α-BHC	27	39	32	10
Dieldrin	27	72	30	8
4,4'-DDE	27	57	19	11
Heptachlor	26	76	35	10

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[a] Swanson, Stephen E., T. Murry Williams, Lloyd M. Petrie, and Earl M. Hansen, "Survey of Analysis of POTW Sludges for Priority Pollutants: Part II Quality Assurance Data," Final Report prepared under EPA Contract No. 68-01-5915, Task 35 (1981).

[b] Minimum spike level 125 μg/ℓ; maximum spike level 1,250 μg/ℓ.

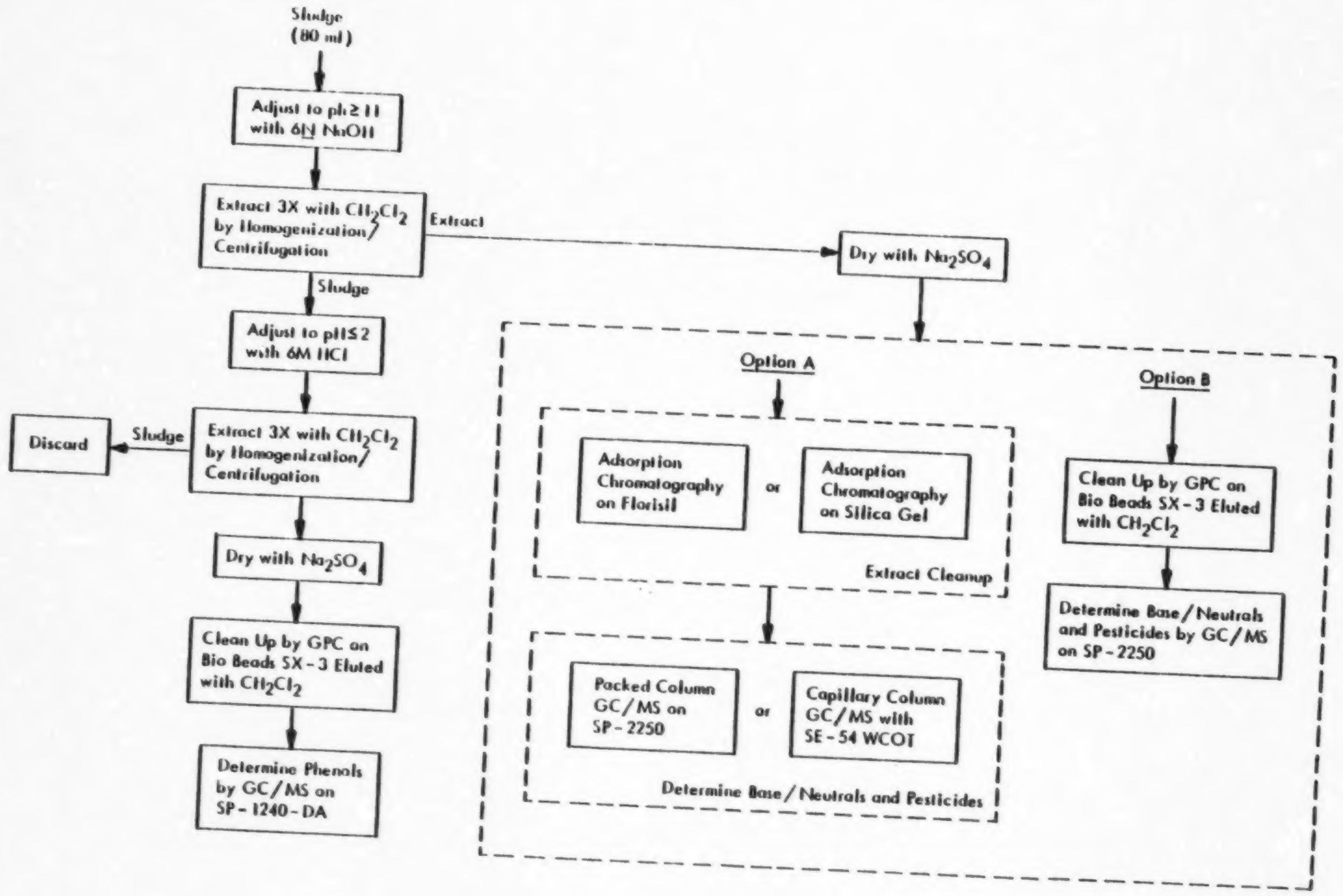
Sludge (80 ml)
Adjust to pH≥11 with 6N NaOH
Extract 3X with CH2Cl2 by Homogenization/ Centrifugation
Extract
Sludge
Adjust to pH≤2 with 6M HCl
Extract 3X with CH2Cl2 by Homogenization/ Centrifugation
Sludge
Discard
Dry with Na2SO4
Clean Up by GPC on Bio Beads SX-3 Eluted with CH2Cl2
Determine Phenols by GC/MS on SP-1240-DA
Dry with Na2SO4
Option A
Adsorption Chromatography on Florisil
or
Adsorption Chromatography on Silica Gel
Extract Cleanup
Packed Column GC/MS on SP-2250
or
Capillary Column GC/MS with SE-54 WCOT
Determine Base/Neutrals and Pesticides
Option B
Clean Up by GPC on Bio Beads SX-3 Eluted with CH2Cl2
Determine Base/Neutrals and Pesticides by GC/MS on SP-2250

Figure 1. Scheme for analysis of extractable organics in sludge.

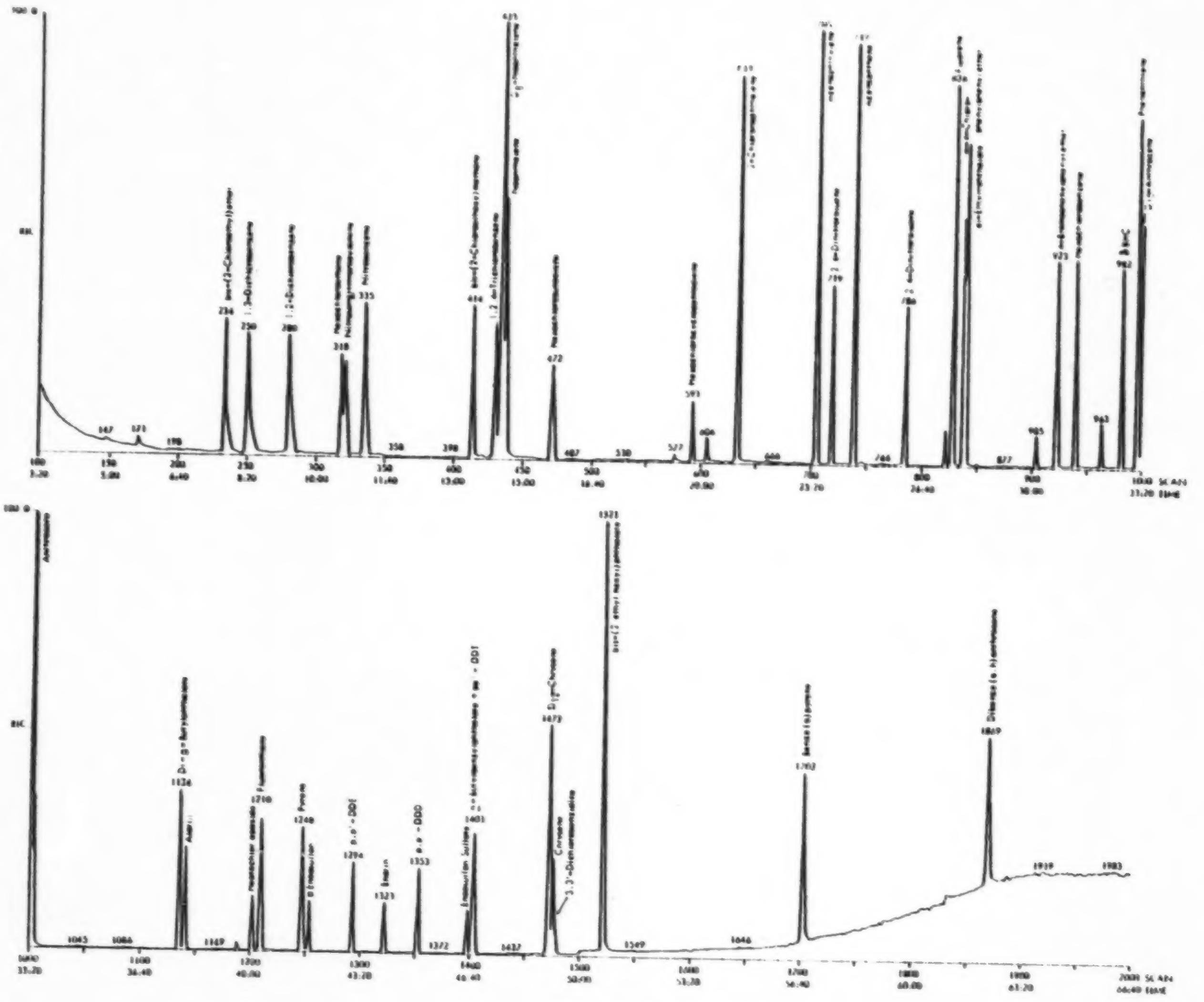

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Figure 2. GC/MS chromatogram of base/neutral compounds on a fused silica capillary column.

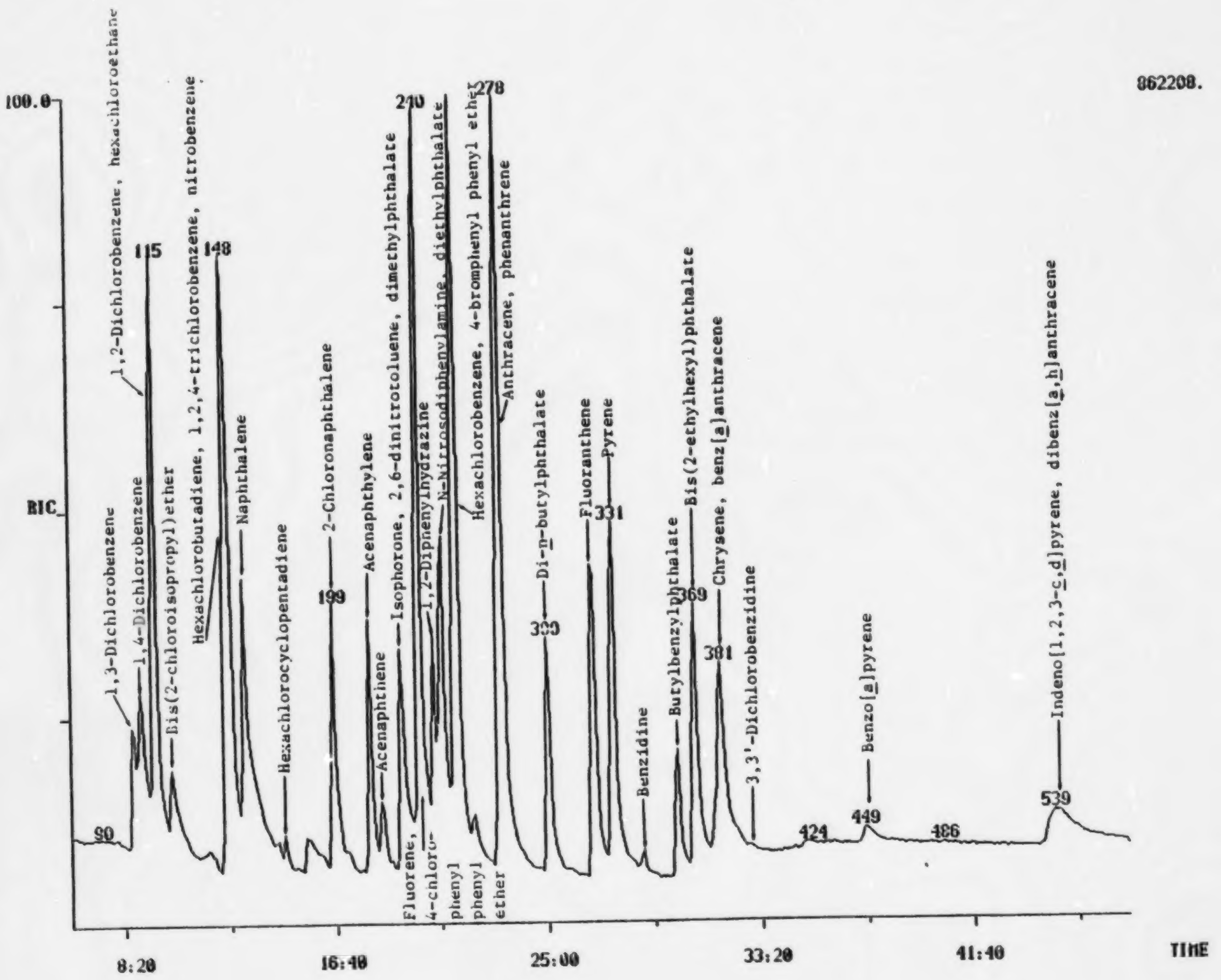

Figure 3. GC/MS chromatogram for the base/neutral compounds on a packed column.

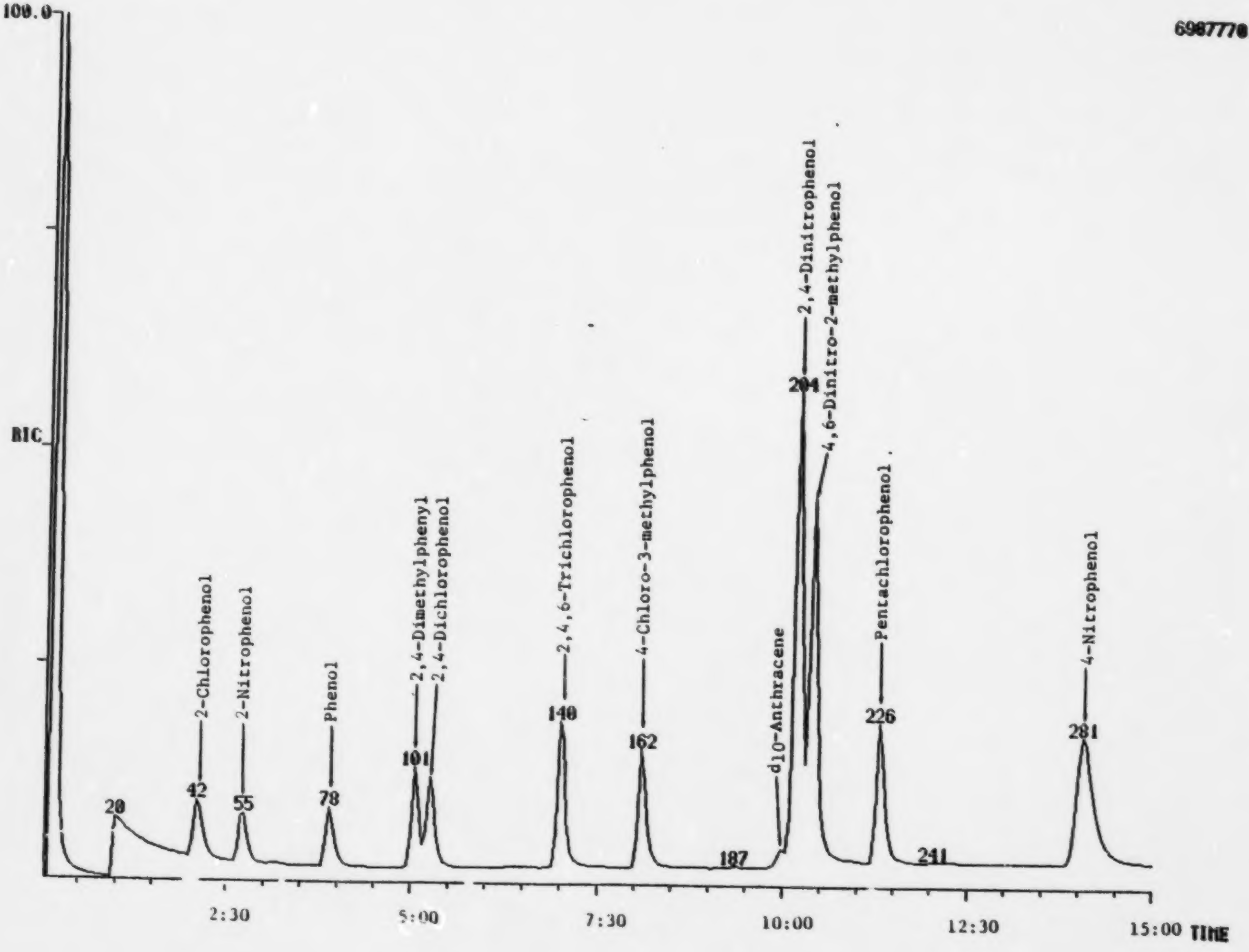

Figure 4. GC/MS chromatogram of the acidic compounds.